Structural Characterization of Zinc and Cadmium Complexes Derived from *N*-(4-carboxybenzyl)pyridinium: Revisiting the Structure of $(Cbp)_2ZnBr_2$ and Influence of the Metal on Carboxylate Coordination Mode‡

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Abstract: The molecular structures of the zinc and cadmium compounds, $(Cbp)_2ZnBr_2$ and $(Cbp)_2CdBr_2$, which feature a zwitterionic ligand derived from *N*-(4-carboxybenzyl)pyridinium, have been determined by using X-ray diffraction. Comparison of the structures of $(Cbp)_2ZnBr_2$ and $(Cbp)_2CdBr_2$ demonstrates that whereas the zinc compound adopts unidentate coordination of the carboxylate ligand, the cadmium counterpart exhibits anisobidentate coordination. The Zn–Br [2.4339(8) Å] and Cd–Br [2.6357(6) Å] bond lengths differ by 0.20 Å which is in accord with the difference in covalent radii of zinc and cadmium (0.22 Å); as such, it suggests that the previous structure of "$(Cbp)_2ZnBr_2$", which possesses a Zn–Br bond length of 2.635(2) Å, actually corresponds to that of $(Cbp)_2CdBr_2$.

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‡ Dedicated with respect to Professor Arnold L. Rheingold in recognition of his valuable contributions to inorganic chemistry throughout his career and for his invaluable help and advice.

INTRODUCTION

The incorporation of charged moieties into molecules provides a means to modulate the electronic properties of ligands derived therefrom. For example, the formal replacement of carbon by boron affords anionic versions of otherwise neutral (i) mono, bis and tris(phosphine) donors,[1,2,3,4,5,6] (ii) poly(pyrazolyl) donors[7,8,9] and (iii) poly(thioether)[10] and poly(thione) donors.[11-16] As a consequence of this substitution, whereas neutral tris(phosphine) molecules,[17] *e.g.* triphos, $MeC(CH_2PPh_2)_3$, are characterized as L_3 donors according to the covalent bond classification,[18] variants such as $[PhB(CH_2PPh_2)_3]^-$, which exist as anions in their closed form, are characterized as L_2X.

Carboxylates are examples of anionic ligands that feature prominently in inorganic chemistry[19] and serve as either X or LX donors to a single metal center depending on whether the coordination is unidentate or bidentate.[20,21] Neutral versions of carboxylates that are zwitterionic (betaines) are also known (Figure 1), as illustrated by derivatives that feature quaternary ammonium,[22] pyridinium,[22a,23,24] or phosphonium[25] centers,[26] and these substituents have been demonstrated to impact the pK_a of the carboxylic acids.[27,28] By comparison to their anionic versions, however, neutral carboxylate ligands have received relatively little attention, although some derivatives have been employed for the synthesis of metal complexes that are inhibitors of topoisomerase II,[29] while dicarboxylate versions have been used to synthesize coordination polymers and metal-organic frameworks.[30,31]

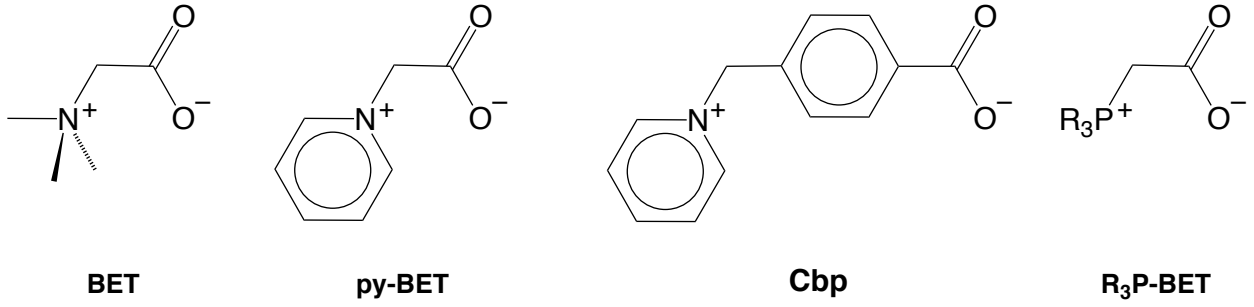


Figure 1. Neutral zwitterionic carboxylate ligands.

Here we describe the use of the deprotonated form of *N*-(4-carboxybenzyl)pyridinium,[32] i.e. the Cbp ligand[24,27] (Figure 1), to afford the zinc and cadmium compounds, $(Cbp)_2ZnBr_2$ and $(Cbp)_2CdBr_2$, and thereby demonstrate how the coordination mode of this carboxylate ligand differs for these two metals. In addition, we provide a re-evaluation of the previously reported structure of the zinc complex, $(Cbp)_2ZnBr_2$.[24a,33]

RESULTS AND DISCUSSION

1. Analysis of the Molecular Structure of Reported $(Cbp)_2ZnBr_2$

Several metal complexes containing the Cbp ligand have previously been synthesized *via* the reactions of (CbpH)Br[27] with a metal salt in the presence of NaOH.[24] Of these compounds, the identity of the zinc complex $(Cbp)_2ZnBr_2$ was determined by using X-ray diffraction (Figure 2).[24a,33] However, examination of the structure reported for $(Cbp)_2ZnBr_2$ reveals several unusual features. Firstly, the Zn–Br bond lengths of 2.635(2) Å are significantly longer than the average terminal Zn–Br bond length of 2.374 Å for tetrahedral zinc compounds listed in the Cambridge Structural Database (CSD);[34] moreover, the average terminal Zn–Br bond length for all compounds listed in the CSD is 2.377 Å. In addition to the anomalous Zn–Br bond length for $(Cbp)_2ZnBr_2$, the Zn–O bond length of 2.265(10) Å is also considerably longer than that observed for other zinc carboxylate complexes. For example, the average Zn–O bond length for four coordinate zinc carboxylate compounds listed in the CSD is 1.957 Å.

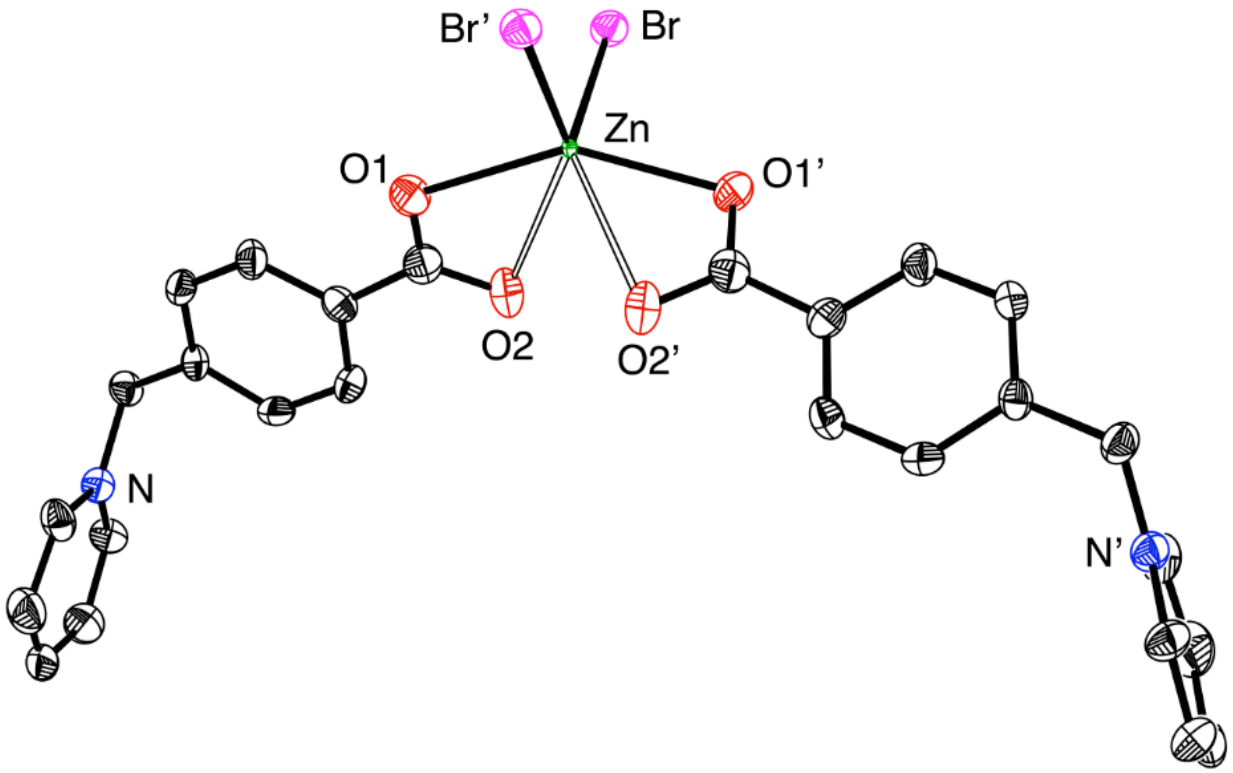
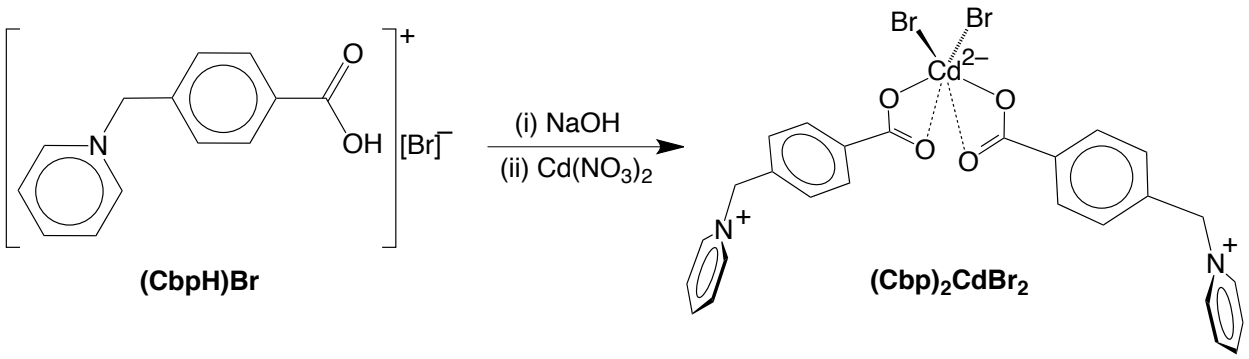


Figure 2. Atom displacement plot for $(Cbp)_2ZnBr_2$ with data taken from CCDC #804539.[24a,33] Note that the displacement parameters for Zn are very small relative to other atoms .

Additional to the unusual Zn–Br and Zn–O bond lengths for $(Cbp)_2ZnBr_2$, a second anomalous feature pertains to the atom displacement parameters associated with the zinc relative to other atoms in the molecule. Specifically, the U_{eq} value for the zinc atom is 0.0128(3) Å^2, which is significantly smaller than those of neighboring atoms. For example, the oxygen atoms bound to the zinc center possess U_{eq} values of 0.060(3) Å^2 and 0.064(3) Å^2, while the bromine atoms have U_{eq} values of 0.0446(4) Å^2. This difference in atomic displacement parameters is also apparent by visual examination of atom displacement plot of the deposited data (Figure 2), which suggests that, in tandem with the aforementioned bond length anomaly, that the atom that has been assigned as zinc is actually an element with a larger atomic number.[35] Therefore, we considered the possibility that the atom in question is actually that of its Group 12 congener, namely cadmium.

2. Synthesis and Structural Characterization of $(Cbp)_2CdBr_2$

To address the possibility that the reported structure $(Cbp)_2ZnBr_2$ corresponds to that of the cadmium complex, $(Cbp)_2CdBr_2$, the latter was synthesized *via* the reaction of $Cd(NO_3)_2 \cdot 4H_2O$ with a neutralized aqueous solution of (CpbH)Br (Scheme 1) and the molecular structure was determined by using X-ray diffraction, as illustrated in Figure 3.



Scheme 1.

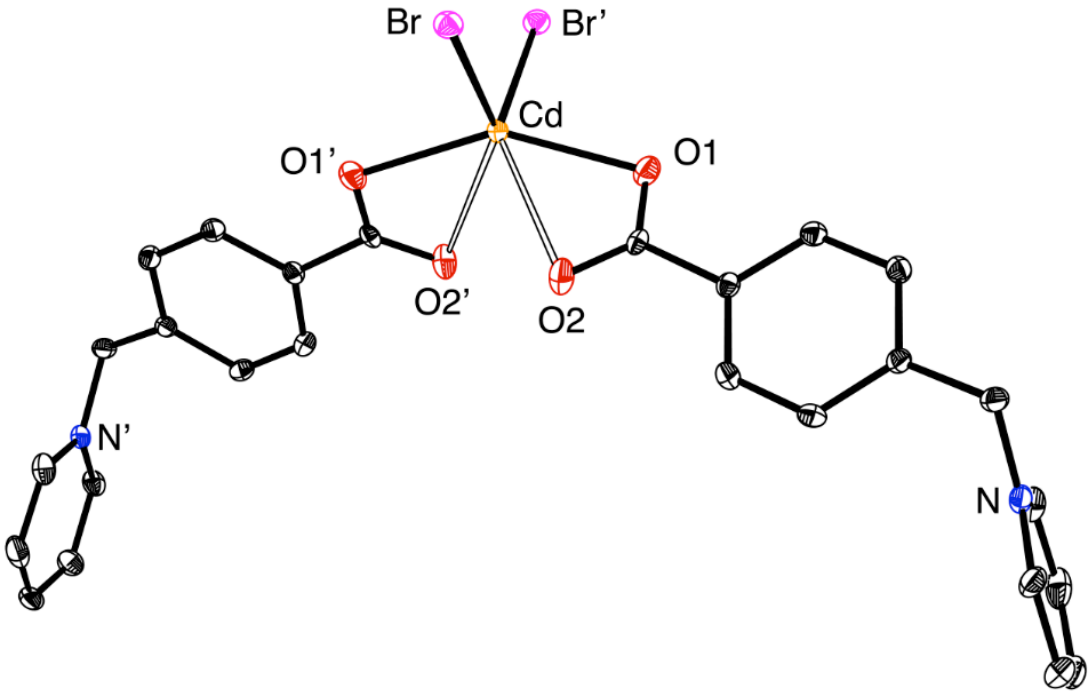


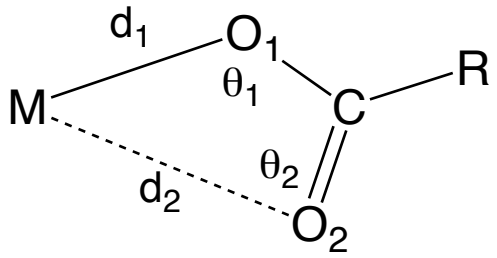
Figure 3. Molecular structure of $(Cbp)_2CdBr_2$.

The metrical data for $(Cbp)_2CdBr_2$ (Table 1) are in accord with other cadmium compounds that feature terminal bromide and carboxylate ligands. For example, the Cd–Br bond lengths of 2.6359(8) Å are comparable to the corresponding average value of 2.578 Å for tetrahedral cadmium complexes listed in the CSD. With respect to the carboxylate coordination, such ligands can bind to a single metal center *via* bidentate, anisobidentate or unidentate coordination modes. These coordination modes may be classified according to the magnitude of the difference in M–O bond lengths (Δd) and M–O–C bond angles ($\theta\theta$), as illustrated in Figure 4 and Table 2.[21,36] On this basis, the carboxylate coordination mode in $(Cbp)_2CdBr_2$, with Cd–O bond lengths of 2.269(3) Å and 2.614(3) Å, and a difference of 0.345 Å, may be classified as anisobidentate, a mode that is well precedented for cadmium (Table 3).[37-42]

Table 1. Selected metrical data for $(Cbp)_2CdBr_2$ and the literature structure of "$(Cbp)_2ZnBr_2$".[24a,33]

	$(Cbp)_2CdBr_2$	"$(Cbp)_2ZnBr_2$"[a]	Δ (Cd – Zn)
d(M–Br) / Å	2.6357(6)	2.635(2)	0.0007
d(M–O1) / Å	2.269(3)	2.265(10)	0.004
d(M•••O2) / Å	2.614	2.626	–0.012
Br–M–Br / °	107.07(3)	106.58(11)	0.49
O1–M–Br / °	92.19(7)	93.2(3)	–1.01,
	106.69(7)	105.6(3)	1.09

(a) Data taken from references 24a,33.



$$\Delta d = d_2 - d_1$$

$$\Delta\theta = \theta_1 - \theta_2$$

Figure 4. Classification of carboxylate coordination modes to a single metal center in which the secondary oxygen atom is proximal.

Table 2. Classification of carboxylate coordination modes to a single metal center in which the secondary oxygen atom is proximal.

Coordination mode	Δd/Å	$\Delta\theta$/°
unidentate	> 0.6	> 28
anisobidentate	0.3 – 0.6	14 – 28
bidentate	< 0.3	< 14

Table 3. Examples of cadmium carboxylate complexes with anisobidentate coordination.

	d(Cd–O1) / Å	*d*(Cd•••O2) / Å	Δ*d* / Å	Δθ / °	Ref.
$(Cbp)_2CdBr_2$	2.269	2.614	0.345	15.0	this work
$[Cd(L1)Cl_2]_n$ [a]	2.286	2.666	0.380	17.1	37
$[Cd(L1)Br_2]_n$ [a]	2.236	2.797	0.561	26.5	37
$Cd(O_2CMe)_2(H_2O)_3$	2.198	2.674	0.476	21.2	39
[Cd(HTTTA)(2,2′-bpy)$(H_2O)_3$]$_n$ [b]	2.286	2.711	0.425	21.5	40
[Cd(BIDPE)(5-OH-bdc)]$_n$ [c]	2.209	2.587	0.378	17.7	41
$[Cd(L2)I_2]_n$ [d]	2.61	2.26	0.35	17	42

(a) L1 = $[CH_2CH(C_5H_5N^+)CO_2^-]_2$.

(b) H_3TTTA = 2,2′,2″-[1,3,5-triazine-2,4,6-triyltris(thio)]-tris-acetic acid.

(c) BIDPE = 4,4′-bis(imidazole-1-yl)diphenyl ether; 5-OH-H_2bdc = 5-hydroxy-isophthalic acid.

(d) L2 = $(CH_2CH_2)_3(N^+CH_2CO_2^-)_2$.

Of more significance than the structure of $(Cbp)_2CdBr_2$ having precedent with related cadmium carboxylate halide complexes, however, is the fact that the metrical data are essentially identical to those reported for the zinc counterpart,[24a,33] as illustrated in Table 1. For example, the Cd–Br bond lengths in $(Cbp)_2CdBr_2$ are 2.6359(8) Å, almost identical to the Zn–Br bond lengths of 2.635(2) Å reported for $(Cbp)_2ZnBr_2$.[24a,33]

In view of the fact that zinc and cadmium have covalent radii (r_{Zn} = 1.22 Å, r_{Cd} = 1.44 Å) that differ by 0.22 Å,[43] the extremely close similarity between the metrical data of $(Cbp)_2CdBr_2$ and those reported for the $(Cbp)_2ZnBr_2$[24a,33] strongly supports the notion that the structure reported for the latter actually corresponds to the cadmium complex

$(Cbp)_2CdBr_2$. Further support that the reported structure of $(Cbp)_2ZnBr_2$ is the cadmium counterpart is provided by refining the crystallographic data for $(Cbp)_2CdBr_2$ as $(Cbp)_2ZnBr_2$, a solution that will be referred to as "$(Cbp)_2ZnBr_2$-***Cd***" (Figure 5).

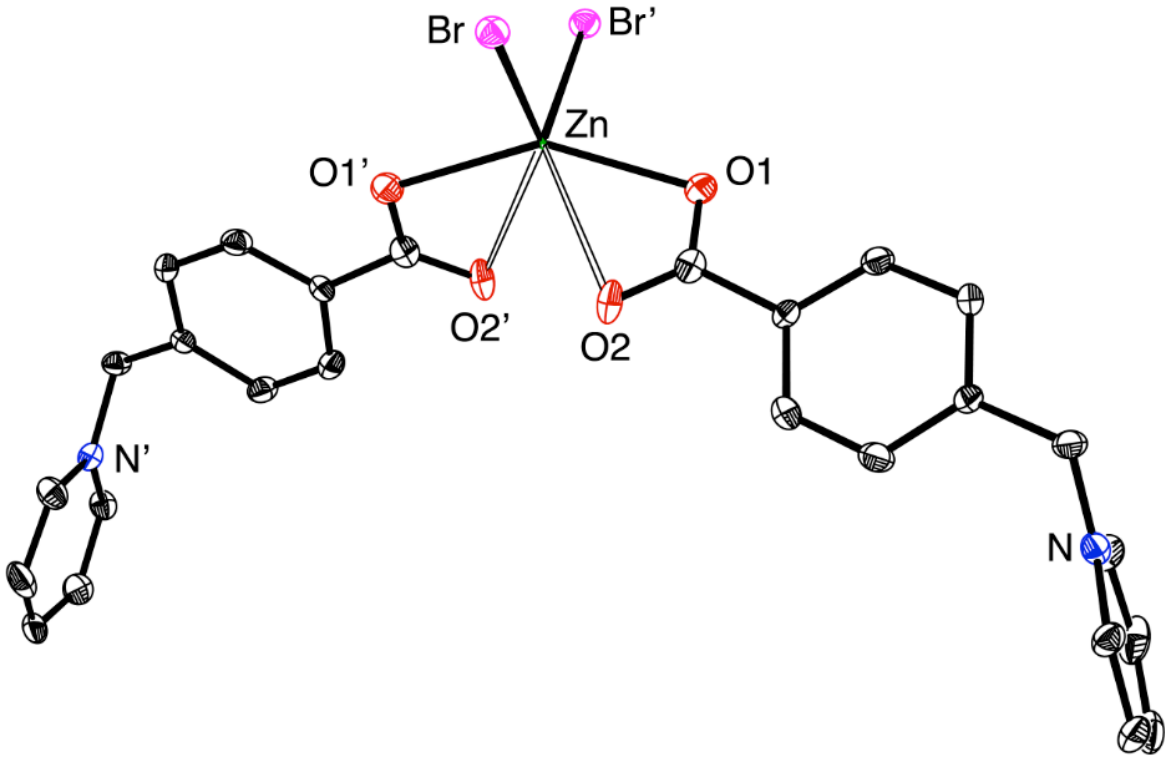


Figure 5. Atom displacement plot for $(Cbp)_2ZnBr_2$-***Cd*** using the experimental data for $(Cbp)_2CdBr_2$.

As would be expected, while the bond lengths for $(Cbp)_2ZnBr_2$-***Cd*** do not differ significantly from that of $(Cbp)_2CdBr_2$, there is an important difference in the atom displacement parameters, and especially those associated with the metal. Thus, while the atom displacement parameters for $(Cbp)_2CdBr_2$ are normal (Figure 3), an anomalously small value is observed for the metal when refined as zinc (Figure 5), as illustrated by the comparison in Figure 6; such change is to be expected because zinc has a lower atomic number than cadmium.[35] For example, whereas U_{eq} for cadmium is 0.01949 Å^2, that for zinc is considerably smaller, with a value of 0.0048 Å^2 (Table 4). In addition to U_{eq} for the zinc being smaller than that for cadmium in the correct structure,

the incorrect inclusion of zinc results in the other atoms having relatively larger U_{eq} values (Table 4).

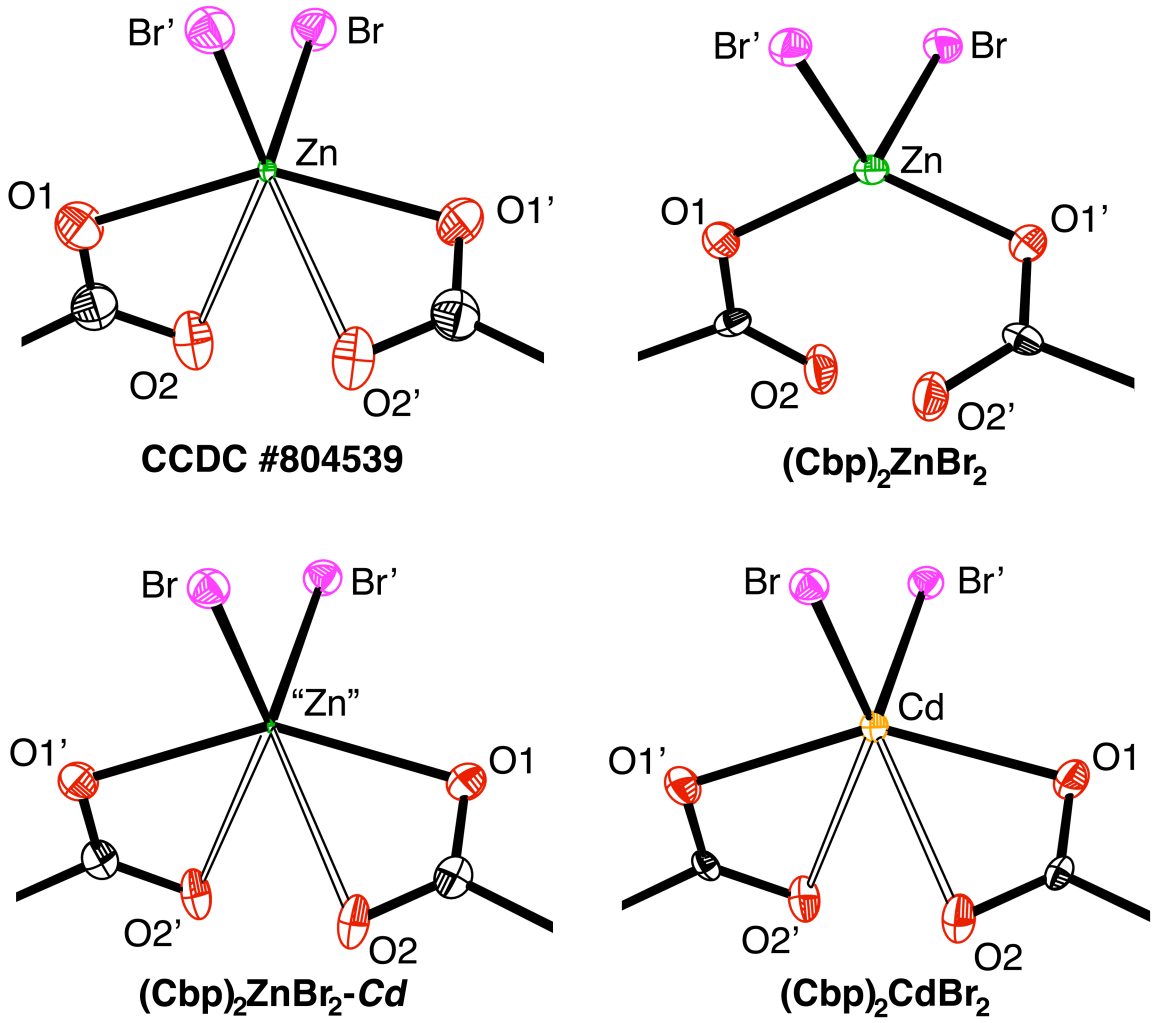


Figure 6. Comparison of the structures of authentic $(Cbp)_2ZnBr_2$ (top right) and $(Cbp)_2CdBr_2$ (bottom right) with incorrect structures for the former (left). The structure on the bottom left, $(Cbp)_2ZnBr_2$-***Cd***, corresponds to the data for $(Cbp)_2CdBr_2$ in which the metal is refined as Zn, thereby resulting in small atom displacement parameters, while that on the top left is the room temperature structure reported for $(Cbp)_2ZnBr_2$,[24a,33] which also exhibits small atom displacement parameters.

Table 4. U_{eq} values (Å^2) for selected atoms for $(Cbp)_2CdBr_2$ with the central atom refined as Cd and as Zn.

	$(Cbp)_2CdBr_2$	$(Cbp)_2ZnBr_2$-*Cd*	$U_{eq}(X)_{Zn/Cd}$ [a]
M	0.01949	0.0048	0.25
Br	0.02608	0.0308	1.18
O1	0.0316	0.0357	1.13
O2	0.0353	0.043	1.2
C1	0.0177	0.029	1.6
C_{av}(ring)	0.0276	0.0335	1.21
C(methylene)	0.0236	0.029	1.2
N	0.0221	0.026	1.18

(a) $U_{eq}(X)_{Zn/Cd} = U_{eq}(X)[(Cbp)_2ZnBr_2\text{-}Cd] / U_{eq}(X)[(Cbp)_2CdBr_2]$

For further comparison, the U_{eq} values for atoms relative to the metal in the different refinement procedures are summarized in Table 5, which illustrates how the non-metal atoms have significantly larger $U_{eq}(X)_{rel}$ values in the incorrect structure. As an illustration, the $U_{eq}(X)_{rel}$ values for the nonmetal atoms in $(Cbp)_2CdBr_2$ range from 0.91 to 1.81, whereas those for the incorrect refinement of $(Cbp)_2ZnBr_2$-*Cd* range from 5.42 to 8.96. Significantly, $U_{eq}(X)_{rel}$ values for the reported structure of "$(Cbp)_2ZnBr_2$" are also large, which again supports the proposal that the metal is not actually zinc.

Table 5. Relative U_{eq} values ($Å^2$)[a] for selected atoms of $(Cbp)_2CdBr_2$, $(Cbp)_2ZnBr_2$ and those for incorrect refinements.

	$(Cbp)_2CdBr_2$	**$(Cbp)_2ZnBr_2$**	**$(Cbp)_2ZnBr_2$-*Cd***	**"$(Cbp)_2ZnBr_2$"[b]**
M	1	1	1	1
Br	1.338	1.295	6.417	3.484
O1	1.621	1.331	7.438	4.688
O2	1.811	1.814	8.959	5.000
C1	0.908	0.943	6.042	3.984
C(ring)	1.414	1.327	6.973	3.949
C(methylene)	1.211	0.924	6.042	3.359
N	1.134	0.973	5.417	3.203

(a) Relative $U_{eq} = U_{eq}(\text{atom})/U_{eq}(\text{M})$.

(b) Data taken from references 24a,33.

3. Synthesis and Structural Characterization of $(Cbp)_2ZnBr_2$

In view of the above discussion, we deemed it essential to determine the molecular structure of $(Cbp)_2ZnBr_2$. Thus, $(Cbp)_2ZnBr_2$ was obtained in a manner analogous to the cadmium counterpart (Scheme 1) and the structure was determined by using X-ray diffraction, as illustrated in Figure 7.

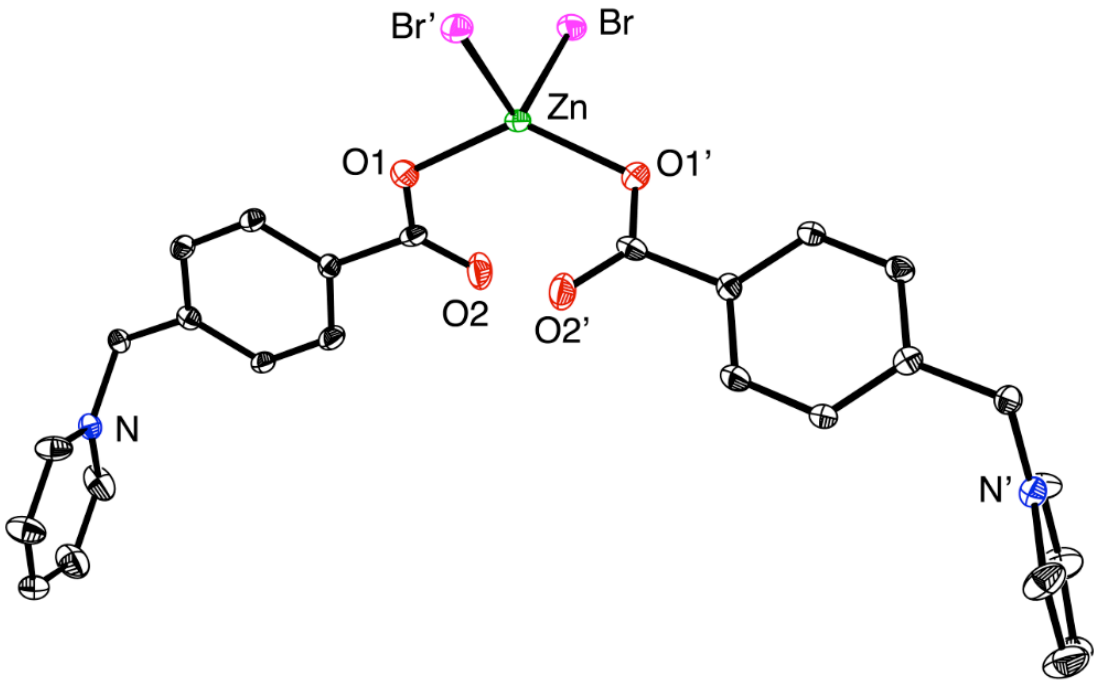


Figure 7. Molecular structure of $(Cbp)_2ZnBr_2$.

Significantly, the structure of $(Cbp)_2ZnBr_2$ differs in some important ways from that previously reported. Firstly, the atomic displacement parameters of the zinc and other atoms (Figure 7) are much more reasonable than those for the previous structure (Figure 2), as compared directly in Figure 6. Thus, when normalized to a value of 1.00 for zinc, the $U_{eq}(X)_{rel}$ values for the nonmetal atoms in $(Cbp)_2ZnBr_2$ range from 0.92 to 1.81, in contrast to the range of 5.42 to 8.96 for the incorrect refinement, $(Cbp)_2ZnBr_2$-***Cd*** (Table 5).

In addition to improved atom displacement parameters, the metal center of $(Cbp)_2ZnBr_2$ exhibits significantly different bond lengths to those previously reported. For example, the Zn–Br bond length of 2.4339(8) Å is not only considerably shorter than the reported value of 2.635(2) Å, but it also corresponds closely to the CSD average of 2.411 Å for zinc carboxylate bromide compounds and 2.374 Å for all tetrahedral zinc bromide compounds. The suggestion that the reported structure for "$(Cbp)_2ZnBr_2$" is actually that of $(Cbp)_2CdBr_2$ rationalizes these differences in bond lengths; otherwise, the two structures of $(Cbp)_2ZnBr_2$ would be classified as bond-stretch isomers, for which

the original examples were shown to be erroneous.[44] The determination of the correct structure for $(Cbp)_2ZnBr_2$ is also noteworthy because otherwise the reported structure for "$(Cbp)_2ZnBr_2$" would lead to the conclusion that coordination of a neutral carboxylate ligand had a much more profound effect on metal-ligand bond lengths than observed for coordination anionic variants. For example, the Zn–Br bond length in an acetate complex, $L_2Zn(O_2CMe)Br$ [2.3463(15) Å][45] is considerably shorter than that reported for "$(Cbp)_2ZnBr_2$".

Table 6. Comparison of the metrical data for $(Cbp)_2ZnBr_2$ with previously reported data.

	$(Cbp)_2ZnBr_2$	**"$(Cbp)_2ZnBr_2$"**[a]	□ [b]
d(M–Br) / Å	2.4339(8)	2.635(2)	0.201
d(M–O1) / Å	1.977(4)	2.265(10)	0.288
d(M•••O2) / Å	2.951	2.626	-0.325
Br–M–Br / °	111.87(5)	106.58(11)	-5.29
O1–M–Br / °	98.68(13)	93.2(3)	-5.5
	107.69(13)	105.6(3)	-2.1

(a) Data taken from references 24a,33.

(b) Difference between previously reported metrical data and those described here.

Another important structural difference between $(Cbp)_2ZnBr_2$ and that previously reported is concerned with the coordination of the carboxylate ligand. Specifically, with Zn–O distances of 1.977 Å and 2.951 Å, the carboxylate ligand of $(Cbp)_2ZnBr_2$ is clearly classified as unidentate (Table 2), whereas the reported structure, with more similar bond lengths of 2.265 Å and 2.626 Å, would be classified as anisobidentate. Examination of the literature indicates that unidentate coordination of carboxylate ligands is typically observed in zinc halide compounds of the type $[Y{\sim}CO_2]ZnX_2$ (Table 7).[22a,23b,46–50]

Table 7. Structural comparison of $(Cbp)_2ZnBr_2$ with similar complexes in which the carboxylate features a pyridinium moiety.

	***d*(M—O_1)/Å**	***d*(M···O_2)/Å**	**Δ*d*/Å**	**Δθ/°**	**Ref.**
$(Cbp)_2ZnBr_2$	1.977	2.951	0.974	47.3	This work
$\{Zn_2(Cbp)_2(BDC)_2(H_2O)_2]\}_n$ [a]	1.985	2.853	0.868	40.6	22a
$Zn(pyBET)_2Cl_2$ [b]	1.988	3.117	1.129	54.9	22a
$ZnCl_2(pyBET)(py)$	1.986	3.000	1.014	47.6	23b
$Zn(pyBET)(H_2O)Cl_2$ [b]	1.936	3.227	1.291	63.9	22a
$[(NH_2C(O)(C_5H_4N)CH_2CO_2]_2ZnCl_2$	2.014	2.898	0.884	41.0	46
$[(NH_2C(O)(C_5H_4N)CH_2CO_2]_2ZnI_2$	2.008	2.878	0.870	39.8	47
$[HO_2CC_2H_2(C_5H_4N)CH_2CO_2]_2ZnCl_2$	1.998	2.956	0.958	45.8	48
$[\{N(C_5H_4)_2NCH_2CO_2\}ZnCl_2]_2$	1.968	3.217	1.249	60.6	49
$Zn(ccop)(H_2O)_5$ [c]	2.028	3.452	1.424	73.9	50

(a) BDC = 1,4-benzenedicarboxylate. (b) pyBET = $C_5H_5N^+CH_2COO^-$. (c) H_2ccop = 5-carboxyl-1-carboxymethyl-2-oxidopyridinium.

To address the significance of the difference in the carboxylate coordination modes in more detail, the distribution of carboxylate coordination modes according to the magnitude of Δd for zinc and cadmium compounds listed in the CSD is presented in Figure 8 and Figure 9. These data clearly indicate that zinc shows a greater tendency than cadmium to adopt unidentate coordination. For example, comparison of pairs of zinc and cadmium carboxylate compounds, $[L]MO_2CR$, that feature the same supporting ligand (Table 8)[51-54] indicate that Δd is consistently larger for the zinc counterpart.[55] Thus, the structure reported for "$(Cbp)_2ZnBr_2$" is also unusual in that it would not be expected to exhibit the same denticity as the cadmium counterpart; as

such, the coordination mode of the carboxylate ligand is further evidence of misassignment of the central atom.

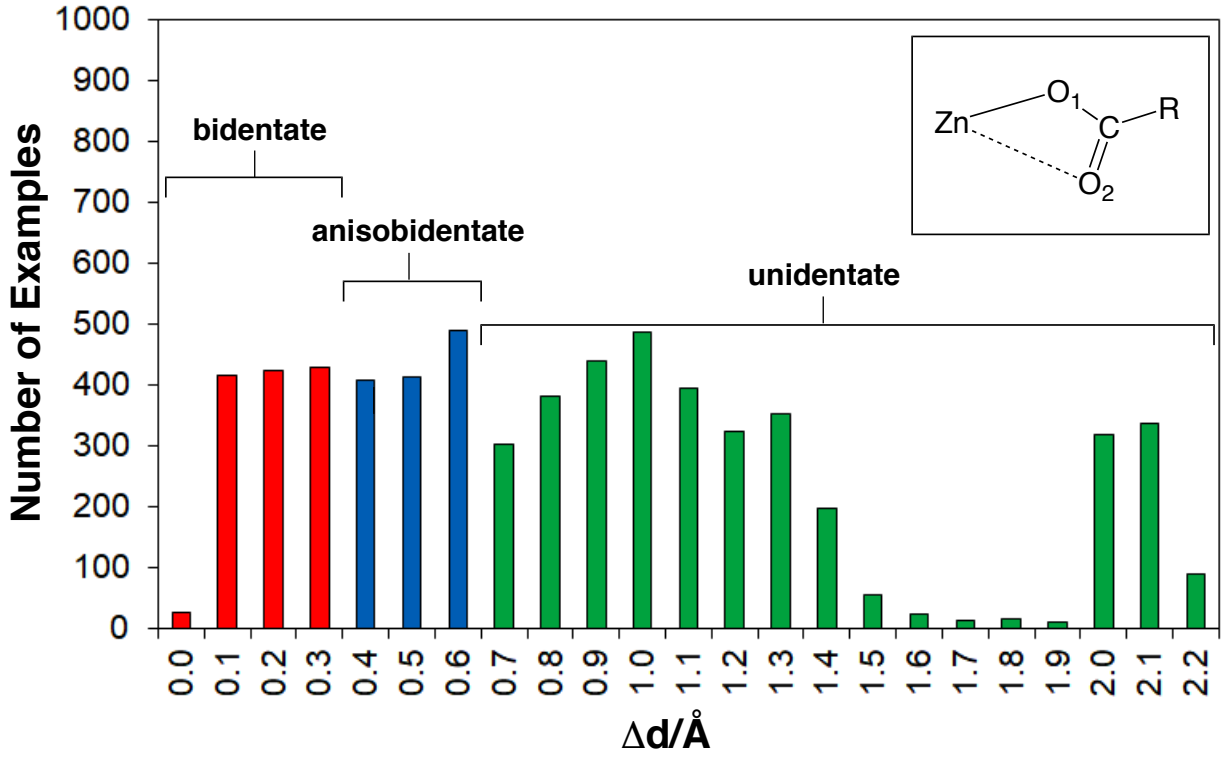


Figure 8. Distribution of Δd, i.e. $d(Zn–O_2) – d(Zn–O_1)$ for nonbridging zinc carboxylate compounds listed in the CSD.

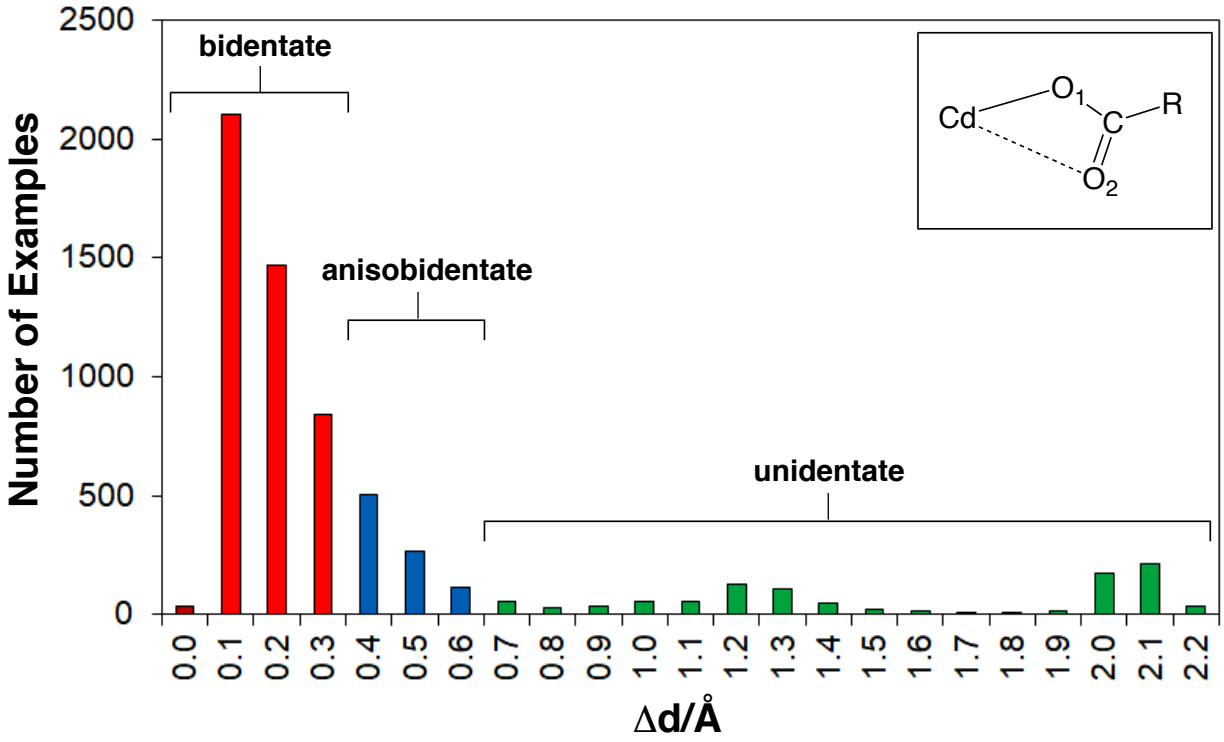


Figure 9. Distribution of □*d*, i.e. *d*(Cd–O_2) – *d*(Cd–O_1) for nonbridging zinc carboxylate compounds listed in the CSD.

Table 8. Structural comparison of zinc and cadmium carboxylate complexes featuring otherwise identical connectivity.

	***d*(M-O1)/Å**	***d*(M···O2)/Å**	**Δ*d*/Å**	**Δθ/°**	**Ref**
$(Cbp)_2ZnBr_2$	1.977	2.951	0.974	47.3	This work
$(Cbp)_2CdBr_2$	2.269	2.614	0.345	15.0	This work
[Tptm]ZnO_2CMe[a]	2.039	2.479	0.440	19.2	51
[Tptm]CdO_2CMe[a]	2.289	2.507	0.218	10.0	52
[Tptm]ZnO_2CH[a]	2.036	2.670	0.634	28.3	51
[Tptm]CdO_2CH[a]	2.316	2.534	0.218	13.8	52
$(2\text{-apy})_2Zn(O_2CC_6H_5)_2$[b]	1.930	2.872	0.942	44.6	53
$(2\text{-apy})_2Cd(O_2CC_6H_5)_2$[b]	2.321	2.429	0.108	4.94	54

(a) [Tptm] = tris(2-pyridylthio)methyl. (b) apy = 2-aminopyridine.

With the correct structure of $(Cbp)_2ZnBr_2$ now available, it is pertinent to consider the incorrect structure of "$(Cbp)_2ZnBr_2$" in terms of the reliability of the determination of atom assignments by using X-ray diffraction. In this regard, it is well known that it is difficult to differentiate pairs of atoms that have similar atomic numbers by using X-ray diffraction,[56] some examples of which include B/C,[57,58] B/N,[59] C/N,[60] C/O,[61] N/O,[57,62,63] O/F,[64,65] Si/Cl,[65] and Cl/S.[66,67] The prevalence of these errors can be attributed to the fact that X-ray diffraction probes electron density, such that atoms that possess similar atomic numbers can be misidentified. Less well known, however, is the fact that misidentification is also possible for atoms with very different atomic numbers. Examples of this phenomenon include the misidentification of Cu as Co,[68] Br as Cu and Ag,[69] O as S,[70] Zn as Mo,[71] Sn as Se,[72] Ni (or Co or Zn) as Pd,[73] Re as Cd,[35] and a combination of Ni/Cl/N being incorrectly refined as Ln/Ni/Cl (Ln = Eu, Ce, Gd).[74] In the present case, Z_{Zn} and Z_{Cd} differ by 18, and thus provides another example of how care must be applied to assigning atoms in structures determined by using X-ray diffraction.

Other evidence that the zinc center of the reported structure of "$(Cbp)_2ZnBr_2$"[24a,33] has been misassigned is provided by a Hirshfeld "rigid-bond" analysis, in which the difference in the mean-square amplitudes along an A–B bond, $\Delta_{AB} = z_A^2 - z_B^2$, is expected to be approximately zero for a well-behaved structure.[75,76,77] For example, the C–C, C–N and C–O bonds in organic compounds are typically characterized by values of Δ_{AB} less than 0.001 Å^2,[75,76] although larger values of approximately 0.003 Å^2 for Δ_{AB} are often typical for metal compounds.[78,79] In this regard, while Δ_{AB} for the Zn–Br bond of $(Cbp)_2ZnBr_2$ (0.0001 Å^2) and the Cd–Br bond of $(Cbp)_2CdBr_2$ (0.0006 Å^2) have values that are within the expected range, that for the Zn–Br bond of the reported structure of "$(Cbp)_2ZnBr_2$" (0.0192 Å^2) well exceeds the expected range and is a factor of approximately 200 greater than that for authentic $(Cbp)_2ZnBr_2$. In addition to the absolute magnitude of Δ_{AB}, values that differ by more than a few standard uncertainties

from zero are considered to be indicative of an erroneous structure.[77] The value of Δ_{AB}/σ for the Zn–Br bond of the reported structure of "$(Cbp)_2ZnBr_2$" has a very large value of 21.3 and thus fails at the 21σ level;[80] in contrast, Δ_{AB}/σ for the Zn–Br bond of authentic $(Cbp)_2ZnBr_2$ is close to zero (0.17) and thus indicative of a correct structure.

Finally, it is pertinent to discuss the impact of the incorrect atom assignment on the *R* value[81] of the refinement because the *R* value is widely adopted as a criterion to evaluate the reliability of a structure determination. In this regard, the *R* value for the structure of $(Cbp)_2ZnBr_2$ reported here is 4.27 %, whereas that for the previously reported structure is 9.40 %.[24a,33] Although the latter *R* value is significantly greater than normally accepted values,[82] it does not, *per se*, indicate that a compound has been incorrectly identified because it is also a reflection of crystal quality. In this regard, 6.8 % of the zinc compounds listed in the CSD have *R* values of 9.00 % or greater and so it alone cannot be used to indicate that the structure corresponds to the correct or incorrect compound. With respect to the impact of refining cadmium as zinc for the structure reported here, the *R* value for the zinc refinement (7.67 %) is distinctly greater than the cadmium refinement (2.50 %), but is not sufficiently high that it would prevent publication if the problem had not been detected. The more telling features that indicate that the structure is incorrect are provided by (i) anomalous bond lengths, (ii) unusual atom displacement parameters, and (iii) large Δ_{AB} and Δ_{AB}/σ values derived by a Hirshfeld analysis.

CONCLUSIONS

In summary, X-ray diffraction studies on the zinc and cadmium compounds, $(Cbp)_2ZnBr_2$ and $(Cbp)_2CdBr_2$, differ with respect to the coordination of the carboxyl groups. Specifically, the zinc compound adopts unidentate coordination of the carboxylate ligand, whereas the cadmium counterpart exhibits anisobidentate coordination. The Zn–Br [2.4339(8) Å] and Cd–Br [2.6357(6) Å] bond lengths in these compounds differ by 0.20 Å which is in accord with the difference in covalent radii of

these metals (0.22 Å). The previously reported Zn–Br bond length of 2.635(2) Å for "$(Cbp)_2ZnBr_2$" is thus anomalous, and the close correspondence with the structure of $(Cbp)_2CdBr_2$ suggests that it is actually that of the cadmium complex. Examination of atom displacement plots and a Hirshfeld analysis of the data confirm this interpretation. As such, while it is well-known that atoms with similar atomic numbers may be difficult to differentiate by using X-ray diffraction, the present study provides another example where atoms with significantly different atomic numbers ($\Delta Z = 18$) may be misidentified.

EXPERIMENTAL SECTION

General Considerations

^{1}H NMR spectra were measured on Bruker 400 Avance III and Bruker 500 DMX spectrometers. ^{1}H chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity (δ 4.79 for DHO).[83] Coupling constants are given in hertz. Infrared spectra were recorded on a Perkin Elmer Spectrum Two spectrometer in attenuated total reflectance (ATR) mode, and are reported in reciprocal centimeters. (CbpH)Br was prepared by the literature method.[27]

X-ray Structure Determinations

X-ray diffraction data were collected on a Bruker Apex II diffractometer. The structures were solved by using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2014/7).[84] The structure of $(Cbp)_2CdBr_2$ was also refined as $(Cbp)_2ZnBr_2$ to illustrate the impact of incorrect atom assignments on the atom displacement parameters and refinement parameters. The Hirshfeld test was performed with PLATON.[77a,b,85] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC #2195189-2195191).

Synthesis of $(Cbp)_2ZnBr_2$

A solution of (CbpH)Br (75 mg, 0.25 mmol) in H_2O (3 mL) was treated with an aqueous solution of NaOH (0.33 M) until a pH of ≈ 7 was obtained, after which $Zn(NO_3)_2 \cdot 6H_2O$ (40 mg, 0.13 mmol) was added. The solution was left to stand at room temperature, thereby resulting in the deposition of crystals of $(Cbp)_2ZnBr_2$ as crystals suitable for X-ray diffraction over a period of two days. The crystals were isolated by decantation, washed with water (2 × 5 mL), and dried. Yield: 23 mg (28%). Anal. Calcd. for $(Cbp)_2ZnBr_2$: C, 47.9%; H, 3.4%; N, 4.3%. Found: C, 47.6%; H, 3.4%, N, 4.3%. ^{1}H NMR (D_2O): 5.87 [s, 4H, $(C_5H_5NC\underline{H}_2C_6H_4CO_2)_2ZnBr_2$], 7.49 [d, J = 8, 4H, $(C_5H_5NCH_2C_6\underline{H}_4CO_2)_2ZnBr_2$], 7.90 [d, J = 8, 4H, $(C_5H_5NCH_2C_6\underline{H}_4CO_2)_2ZnBr_2$], 8.08 [t, J = 7, 4H, $(C_5\underline{H}_5NCH_2C_6H_4CO_2)_2ZnBr_2$], 8.57 [t, J = 8, $(C_5\underline{H}_5NCH_2C_6H_4CO_2)_2ZnBr_2$], 8.92 [d, J = 6, H, $(C_5\underline{H}_5NCH_2C_6H_4CO_2)_2ZnBr_2$]. IR Data (ATR, cm^{-1}): 3130 (w), 3055 (w), 2995 (w), 1640 (m), 1612 (s), 1565 (m), 1510 (w), 1488 (m), 1417 (m), 1362 (s), 1285 (m), 1161 (m), 1109 (m), 1017 (m), 957 (w), 760 (s), 676 (s), 591 (m), 458 (m).

Synthesis of $(Cbp)_2CdBr_2$

A solution of (CbpH)Br (75 mg, 0.25 mmol) in H_2O (3 mL) was treated with an aqueous solution of NaOH (0.33 M) until until a pH of ≈ 7 was obtained, after which $Cd(NO_3)_2 \cdot 4H_2O$ (40 mg, 0.13 mmol) was added, thereby resulting in the rapid deposition of crystals of $(Cbp)_2CdBr_2$. The crystals were isolated by decantation, washed with water (2 × 5 mL), and dried. Yield: 30 mg (34%). Anal. Calcd. for $(Cbp)_2CdBr_2$: C, 44.7%; H, 3.2%; N, 4.0%. Found: C, 44.0%; H, 3.0%; N, 3.8%. ^{1}H NMR (D_2O): 5.93 [s, 4H, $(C_5H_5NC\underline{H}_2C_6H_4CO_2)_2CdBr_2$], 7.55 [d, J = 8, 4H, $(C_5H_5NCH_2C_6\underline{H}_4CO_2)_2CdBr_2$], 7.97 [d, J = 8, 4H, $(C_5H_5NCH_2C_6\underline{H}_4CO_2)_2CdBr_2$], 8.14 [t, J = 7, 4H, $(C_5\underline{H}_5NCH_2C_6H_4CO_2)_2CdBr_2$], 8.63 [t, J = 8, 2H, $(C_5\underline{H}_5NCH_2C_6H_4CO_2)_2CdBr_2$], 8.98 [d, J = 6, 4H, $(C_5\underline{H}_5NCH_2C_6H_4CO_2)_2CdBr_2$]. IR Data (ATR, cm^{-1}): 3127 (vw), 3086 (vw), 3041 (w), 2997 (vw), 1634 (w), 1594 (m), 1546 (s), 1489 (m), 1418 (w), 1388 (s), 1373 (m), 1287 (w), 1217

(w), 1180 (w), 1165 (m), 857 (m), 819 (m), 783 (m), 760 (s), 711 (m), 682 (m), 592 (w), 524 (w), 461 (m).

APPENDIX A. Supplementary Data

Crystallographic data in CIF format (CCDC #2195189-2195191). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.xxxxxx.

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(81) *R* refers to the conventional discrepancy index of $R1 = [\Sigma\,||F_o| - |F_c||]/[\Sigma\,|F_o|]$ for $I > 2\sigma(I)$.

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