Inorganica Chimica Acta, 65 (1982) L87–L89

Cadmium(II) Halide Complexes of Tertiary Phosphines.

Part II.* Structural Variations in the 1:1 Series, $CdX_2(PR_3)$

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Received April 22, 1982

We have recently shown [1] how significant variation in the structures of $HgX_2(PR_3)$ complexes [1–3] can be rationalised in terms of the varying σ-donor strengths of the PR_3 ligands coupled with the tendency for mercury(II) towards linear co-ordination. Cadmium shows no such preference for digonal geometry, and the majority of complexes of the type $CdX_2(L)$, where (L) is a unidentate ligand, for which definitive structural data are available, contain octahedrally co-ordinated Cd atoms [4]. It was therefore of significance to find that the range of structures exhibited by $CdX_2(PR_3)$ adducts is similar to that found for the mercury(II) analogues. The structures which we have characterised by full single-crystal X-ray analysis comprise the centrosymmetric halogen-bridged dimer, $CdI_2(PEt_3)$ [(I), Fig. 1], the discrete tetramer, α-$CdCl_2(PCy_3)$† [(II), Fig. 2], and the pentaco-ordinate polymers, $CdX_2(PMe_2Ph)$ [(III, X = Cl [6], Br or I), Fig. 3].

Although the bromo-analogue of (I) was suggested to be a halogen-bridged dimer from X-ray studies as long ago as 1940 [7], and much supposition has been made on the basis of this early work, the present results represent the first fully authenticated $[CdX_2(L)]_2$ structure. There is no extension beyond the dimer stage, the closest Cd···I inter-dimer distance being greater than 4 Å.

The tetrameric arrangement in (II) is reminiscent of that found [1] in α-$HgCl_2(PBu_3)$, but all the $[Cd_2Cl_2]$ rings are distinctly asymmetric (Fig. 2) and the pattern of ν(CdCl) bands in the far-infrared spectrum shows that the inter-dimer interactions are significant, in contrast with the situation found [3] in α-$HgCl_2(PBu_3)$.

Complexes (III, X = Br or I) have the same polymeric structure as the chloro analogue [6]. Differences in the bridging and terminal Cd–X bond lengths in relation to the sum of the covalent radii can be related to a successive lowering in strength of bridging in the bromide and iodide complexes compared with the chloride.

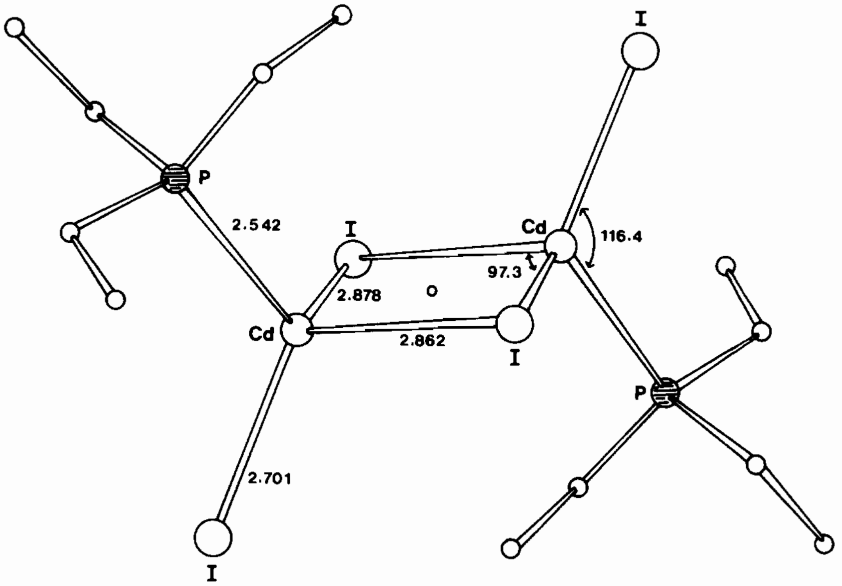

Fig. 1. Molecular structure of $CdI_2(PEt_3)$ (I). *Crystal data*: Monoclinic, a = 8.462(4), b = 10.114(5), c = 15.563(8) Å, β = 95.20(5)°; space group $P2_1/c$, Z = 4; R = 0.0751 for 2941 independent reflections. E.s.d. s are *ca.* 0.001 Å and *ca.* 0.1°.

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*Part I is to be taken to be Ref. 6.

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†Two forms of this formula have been reported [5].

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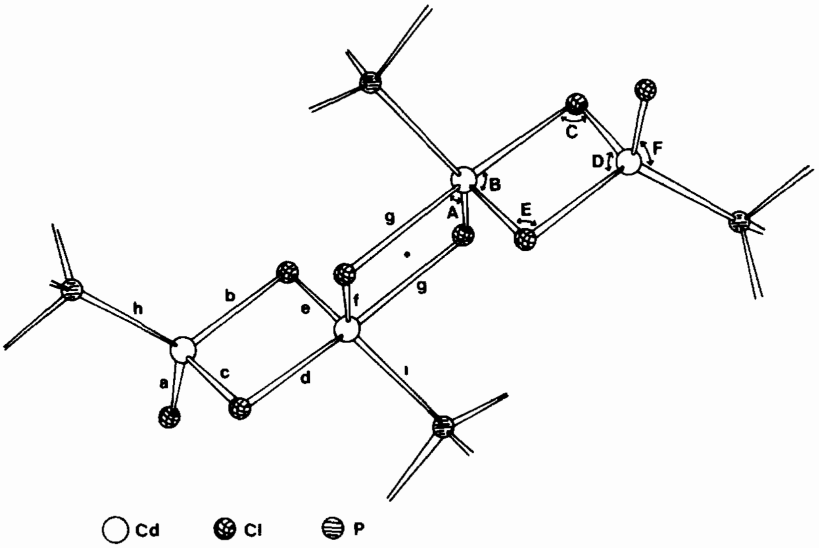

Fig. 2. Molecular structure of α-$CdCl_2(PCy_3)$ (II). *Crystal data*: Monoclinic, a = 14.127(8), b = 16.412(10), c = 19.833(12) Å, β = 113.14(5)°; space group $P2_1/c$, Z = 8; R = 0.046 for 4067 independent reflections. Important parameters: a, 2.422(3); b, 2.538(4); c, 2.487(2); d, 2.801(3); e, 2.520(2); f, 2.465(2); g, 2.832(2); h, 2.569(2); i. 2.553(2) Å; and A, 83.5(1); B, 84.8(1); C, 89.1(1); D, 91.3(1); E, 94.6(1); F, 107.4(1)°.

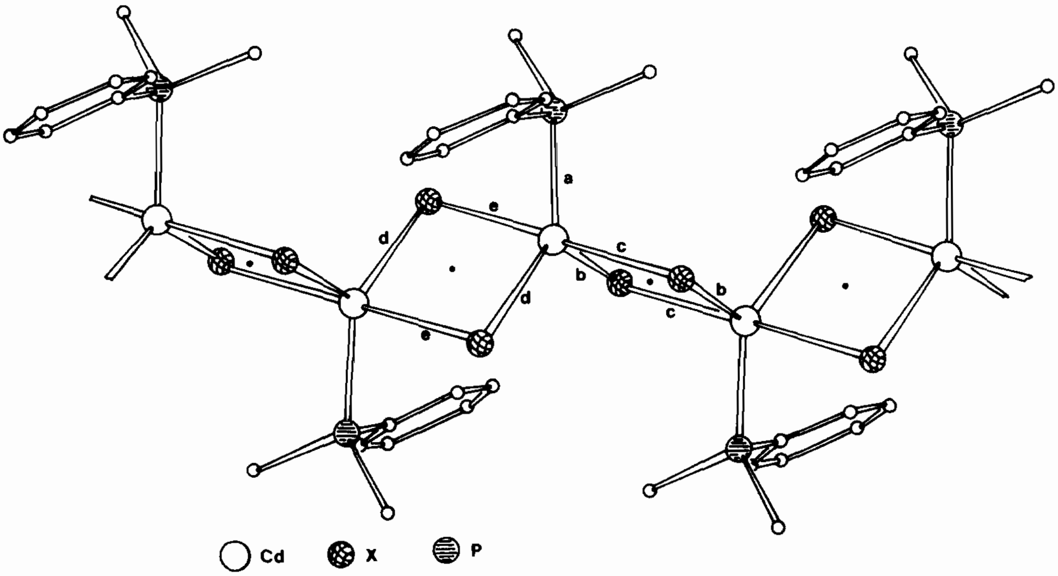

Fig. 3. Molecular structure of $CdX_2(PMe_2Ph)$ (III, X = Br or I). *Crystal data*: Monoclinic; for X = Br: a = 7.361(8), b = 12.599(7), c = 13.012(6) A, β = 93.18(5)°; for X = I: a = 7.839(8), b = 12.868(7), c = 13.526(8) A, β = 94.17(6)°; space group $P2_1/n$, Z = 4; R = 0.067 for 0.098 for 1783 or 2262 independent reflections, for X = Br or I respectively. Important parameters for X = Br or I respectively: a, 2.5 31(4), 2.553(4); b, 2.569(2), 2.768(2); c, 2.915(2), 3.242(2); d, 2.603(2), 2.759(2); e, 2.918(2), 3.201(2) A; and <a–b, 126.9(1), 125.3(1); a–d, 121.8(1), 122.5(1); b–d, 111.3(1), 112.3(1); c–e, 178.7(1), 177.2(1)°.

Using these definitive data, we have developed working correlations between the molecular structure and the low-frequency infrared and Raman spectra, particularly ν(CdX) assignments, and these have enabled us to propose the structures of several other complexes of the $CdX_2(PR_3)$ type to a high degree of confidence. Some of these results are presented in Table I.

It is thus apparent that, as with the $HgX_2(PR_3)$ analogues, the stronger σ-donor ligand (PCy_3 in the

TABLE I. Structures of $CdX_2(PR_3)$ Complexes.

X	$CdX_2(PCy_3)$	$CdX_2(PEt_3)$	$CdX_2(PMe_2PH)$
Cl	$\left\{\begin{array}{l}\text{tetramer}^{a}\\\text{or dimer}\end{array}\right\}^{b}$	polymer	polymer[a]
Br	dimer	polymer	polymer[a]
I	dimer	dimer[a]	polymer[a]

[a]Determined by full X-ray study. [b]Two forms of $CdCl_2$-(PCy_3) exist [5].

phosphine series, I^- in the halide series) encourage a less extended structure. The simplest rationale, applicable to both the Cd and Hg cases, is that the stronger σ-donation from the attached groups the less additional co-ordination there will be. The structural variations now reported are thus likely to be of more general application than was hitherto supposed in the context of the mercury(II) studies.

Acknowledgements

We thank the SERC for a Research Studentship (to TDD) and computing facilities.

References

1 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg Chim. Acta, 43,* 87 (1980).
2 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta, 48,* 185 (1981).
3 N. A. Bell, M. Goldstein, T. Jones, L. A. March and I. W. Nowell, *Inorg Chim. Acta,* in the press.
4 D. G. Tuck, *Rev. Inorg Chem 1,* 209 (1979).
5 F. G. Moers and J. P. Langhout, *Rec. Trav. Chim., 92,* 996 (1973).
6 N. A. Bell, T. D. Dee, M. Goldstein and I. W. Nowell, *Inorg. Chim. Acta, 38,* 191 (1980).
7 R. C. Evans, F. G. Mann, H. S. Peiser and D. Purdie, *J. Chem. Soc.,* 1209 (1940).