Cadmium(II) Complexes containing a Discrete Tetrakis(carboxylato)-bridged Dimetal Core: Isomorphous Dinitratotetrakis(μ-triphenylphosphoniopropionate)dicadmium(II) Dinitrate and Diperchlorate, and Dichlorotetrakis(μ-triphenylphosphoniopropionate)dicadmium(II) Diperchlorate†

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Three cadmium complexes that contain the tertiary phosphine betaine ligand triphenylphosphoniopropionate have been synthesized and structurally characterized by single-crystal X-ray analysis. The complex $[\{Cd[Ph_3P(CH_2)_2CO_2]_2(NO_3)\}_2][NO_3]_2$ **1** belongs to the triclinic space group $P\bar{1}$ with a = 9.152(3), b = 12.833(4), c = 19.278(12) Å, α = 102.25(5), β = 97.20(4), γ = 108.19(5)° and Z = 1; $[\{Cd[Ph_3P(CH_2)_2CO_2]_2(NO_3)\}_2][ClO_4]_2$ **2** is isomorphous with **1** with a = 9.136(6), b = 12.891(2), c = 20.138(5) Å, α = 104.51(1), β = 97.54(4), γ = 107.86(3)°; $[\{Cd[Ph_3P(CH_2)_2CO_2]_2Cl\}_2][ClO_4]_2$ **3** is monoclinic, space group $C2/m$ with a = 9.315(5), b = 37.275(15), c = 13.255(6) Å, β = 112.45(4)° and Z = 2. All three complexes possess a centrosymmetric tetrakis(μ-carboxylato-*O,O'*) dimetal core, the apical sites being occupied by chelating nitrato ions in **1** and **2** and by chloro groups in **3**. In complexes **1** and **2**, the metal atoms are symmetrically bridged by the carboxylato groups, but in **3** the carboxylato group is distorted significantly. The intramolecular Cd···Cd distances are 3.278(2), 3.278(2) and 3.361(2), respectively.

Tetraorganophosphonium salts are known to behave as phase-transfer catalysts and have the ability to alter the surface tension of water.[1] As structural analogues of carboxylic acids, tertiary phosphine betaines, which can be obtained by carboxyalkylation of tertiary phosphines,[2,3] have a molecular skeleton bearing a phosphonium cation and a naked carboxylate group. Upon co-ordination to metal centres, they function like amino acids and tertiary amine betaines which commonly act as zwitterionic species in ligation.[4–13] On the other hand, as phosphorus can utilize its 3d orbitals in bonding to other elements,[14] it can be expected that its co-ordination behaviour towards metal ions will be somewhat different from that of the amino acids and tertiary amine betaines.

Cadmium(II) forms a variety of complexes with carboxylate-like ligands. The crystal structures of a number of simple carboxylates, as well as complexes with amino acids and tertiary amine betaines, have been determined, most of which show one- and three-dimensional arrangements of carboxylate groups bridging adjacent Cd atoms.[15,16] On the other hand, cadmium(II) complexes containing discrete species are rare.[17,18] In order to synthesize complexes of this type, we decided to make use of triphenylphosphoniopropionate, which has a bulky cationic terminal group, as a ligand to test the effect of large steric hindrance on the resulting structures of the cadmium(II) carboxylates.

The tetrakis(μ-carboxylato) dimetal complexes, although first prepared in 1844 as chromium(II) acetate monohydrate, were not documented until the 1953 structural determination of copper(II) acetate monohydrate.[19] Since then the tetrakis(μ-carboxylato-*O,O'*) dimetal complexes of many transition elements such as Cu^{II}, Cr^{II}, Rh^{II} and Mo^{II} have been prepared and fully characterized by a variety of physical methods to elucidate the nature of the metal–metal multiple bond.[20,21] For cadmium(II) carboxylates, to our knowledge, $[\{Cd(CF_3CO_2)_2(PPh_3)\}_2]$ is the only authenticated example that possesses a paddle wheel-like tetrakis(μ-carboxylato)-bridged dimetal core.[18] In the present study, three complexes containing the tetrakis(μ-carboxylato)dicadmium framework, namely $[\{Cd[Ph_3P(CH_2)_2CO_2]_2(NO_3)\}_2][NO_3]_2$ **1**, $[\{Cd[Ph_3P(CH_2)_2CO_2]_2(NO_3)\}_2][ClO_4]_2$ **2** and $[\{Cd[Ph_3P(CH_2)_2CO_2]_2Cl\}_2][ClO_4]_2$ **3**, with triphenylphosphoniopropionate functioning as a carboxylate-like ligand, have been synthesized. Single-crystal X-ray analysis has shown that complexes **1** and **2** have NO_3 as a chelating axial ligand for cadmium(II) in six-co-ordination, whereas Cl^- serves as an axial ligand and cadmium(II) is five-co-ordinated in complex **3**.

Experimental

Materials and Measurements.—Cadmium(II) perchlorate was prepared by the reaction of CdO with $HClO_4$ (70%), triphenylphosphine and cobalt(II) chloride hexahydrate were purchased from E. Merck, cadmium(II) nitrate tetrahydrate from Hopkin & Williams and acrylic acid from Riedel-de Haën. Inrared spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 205 FT-IR spectrometer. The proton NMR spectrum was measured on a Bruker Cryospec WM 250 (250 MHz) spectrometer.

CAUTION: Metal perchlorates are potentially explosive in reactions with organic ligands. Only small amounts should be prepared and handled with great care.

Preparation of Compounds.—The ligand $Ph_3P^+(CH_2)_2CO_2^-$ (L) was prepared by a literature method.[2] ^1H NMR: δ 7.63 (m, 15 H, H-phenyl), 3.40 (m, 2 H, β-H of carboxylate), 2.47

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Crystallographic data for complexes **1**–**3**

Formula	$[\{CdL_2(NO_3)\}_2][NO_3]_2$	$[\{CdL_2(NO_3)\}_2][ClO_4]_2$	$[(CdL_2Cl)_2][ClO_4]_2$
M	1810.2	1885.0	1831.9
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/m$
Crystal size/mm	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.20	0.24 × 0.30 × 0.36
a/Å	9.152(3)	9.136(6)	9.315(5)
b/Å	12.833(4)	12.891(2)	37.275(15)
c/Å	19.278(12)	20.138(5)	13.255(6)
α/°	102.25(5)	104.51(1)	90
β/°	97.20(4)	97.54(4)	112.45(4)
γ/°	108.19(5)	107.86(3)	90
U/Å^3	2052(2)	2129(1)	4252(3)
Z	1	1	2
D_c/g cm^{-3}	1.46	1.47	1.55
$F(000)$	924	960	1864
μ/cm^{-1}	0.67	0.71	0.77
Transmission coefficients	0.96–1.00	—	0.85–0.95
2θ Range/°	5–50	2–50	3–50
Unique data measured	7234	7255	3840
No. of data used, n	4560 [$I > 4\sigma(I)$]	3857 [$I > 6\sigma(I)$]	2437 [$I > 6\sigma(I)$]
No. of variables, p	515	520	255
R*	0.055	0.057	0.057
R'*	0.066	0.068	0.088
S*	1.85	1.17	0.89

* $R = \Sigma\Delta/\Sigma|F_o|$, $R' = [\Sigma w\Delta^2/\Sigma|F_o|^2]^{\frac{1}{2}}$ and $S = [w\Delta^2/(n-p)]^{\frac{1}{2}}$ where $w = [\sigma^2(F_o) + K|F_o|^2]^{-1}$, $\Delta = ||F_o| - |F_c||$; $10^4\ K = 1$, 12 and 80 for complexes **1**, **2** and **3** respectively. Extinction parameter $\chi = 0.000\,57$, $0.001\,29$ and $0.000\,05$ for complexes **1**, **2** and **3** respectively where $F_{corr} = F_c(1 + 0.002\chi F_c^2/\sin 2\theta)^{\frac{1}{4}}$.

(m, 2 H, α-H of carboxylate). IR: 1591s (carboxylate ν_{asym}), 1377s (carboxylate ν_{sym}), 1583s [phenyl ν(C–C)], 1485w [phenyl ν(C–C)], 1438m [phenyl ν(C–C)], 1377s [phenyl ν(C–C)] and 1112s cm^{-1} (phenyl C–H in-plane bending).

$[\{Cd[Ph_3P(CH_2)_2CO_2]_2(NO_3)\}_2][NO_3]_2$ **1**. To cadmium(II) nitrate tetrahydrate (308 mg, 1.0 mmol) dissolved in distilled water (5 cm^3) was added L (324 mg, 1.0 mmol), and the clear solution obtained was heated at *ca.* 60 °C and evaporated until the volume was reduced to about 3 cm^3. After the resulting solution was allowed to stand for one day, colourless plate-like crystals of **1** were obtained. IR: 1645s (carboxylate ν_{asym}), 1396s (carboxylate ν_{sym}), 1588m [phenyl ν(C–C)], 1484m [phenyl ν(C–C)], 1441s [phenyl ν(C–C)], 1281–1357s [multiplet, overlap of phenyl C–H in-plane bending and nitrato ν(N–O)], 1112s (phenyl C–H in-plane bending) and 831m cm^{-1} [ν(N–O)].

$[\{Cd[Ph_3P(CH_2)_2CO_2]_2(NO_3)\}_2][ClO_4]_2$ **2**. When cadmium(II) perchlorate (320 mg, 1.0 mmol) and L (336 mg, 1.0 mmol) were each dissolved in distilled water and mixed, a white precipitate formed immediately. The precipitate was then filtered off, washed with water and dissolved in dimethylformamide (dmf). To this solution calcium(II) nitrate tetrahydrate (308 mg, 1.0 mmol) was added and stirred for about 10 min at *ca.* 50 °C. After the clear solution was allowed to stand for two weeks, colourless prismatic crystals of **2** were obtained. IR: 1643s (carboxylate ν_{asym}), 1393s (carboxylate ν_{sym}), 1587m [phenyl ν(C–C)], 1486m [phenyl ν(C–C)], 1439s [phenyl ν(C–C)], 1112s (phenyl C–H in-plane bending), 1087s [perchlorate ν(Cl–O)] and 624m cm^{-1} [perchlorate ν(Cl–O)].

$[\{Cd[Ph_3P(CH_2)_2CO_2]_2Cl\}_2][ClO_4]_2$ **3**. To a mixture of cadmium(II) perchlorate (160 mg, 0.5 mmol), cobalt(II) nitrate hexahydrate (180 mg, 0.5 mmol) and compound L (668 mg, 2.0 mmol), distilled water (3 cm^3) was added with stirring. A white precipitate formed immediately, and then dmf (*ca.* 2 cm^3) was added and stirred at *ca.* 50 °C until the precipitate dissolved completely. After the clear solution obtained was allowed to stand for several days, colourless prismatic crystals of compound **3** were obtained. IR: 1648s (carboxylate ν_{asym}), 1587m (phenyl C–H in-plane bending), 1440s (phenyl C–H in-plane bending), 1395s (carboxylate ν_{sym}), 1112s (phenyl C–H in-plane bending), 1087s [perchlorate ν(Cl–O)] and 623m cm^{-1} [perchlorate ν(Cl–O)].

Crystallographic Data Collection and Structure Determination.—Information concerning crystallographic data collection and structure refinement is summarized in Table 1. The intensities of **1**, **2** and **3** were collected in the ω-scan mode[22] on a Rigaku AFC7R, a Nicolet R3m/V and a Siemens P4/PC diffractometer, respectively, using Mo-Kα radiation (λ = 0.710 73 Å) at 293 K. Unit-cell parameters were calculated from least-squares fitting of the 2θ angles for 20 selected strong reflections. Crystal stability was monitored by recording two or three check reflections at intervals of 120 data measurements, and no significant variation was detected. An empirical absorption correction based on ψ-scans were applied to the intensity data processing for complexes **1** and **3**.

The structures of all three complexes were solved by a combination of direct methods and Fourier difference syntheses. All non-hydrogen atoms other than the disordered oxygen atoms of the perchlorate group were refined anisotropically by full-matrix least squares. The hydrogen atoms of the ligands were placed in their calculated positions with C–H = 0.96 Å, assigned fixed isotropic thermal parameters, and allowed to ride on the respective parent carbon atoms. The contributions of these hydrogen atoms were added to the structure-factor calculations, but their positions were not refined. In both complexes **2** and **3**, the perchlorate ion exhibits two-fold orientational disorder, and distance restraints of Cl–O = 1.38 ± 0.02 and O···O = 2.24 ± 0.02 Å were applied in refinement.

All calculations were carried out on a PC 486 computer using the SHELXTL PC program package.[23] Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[24] Final atomic coordinates for the three crystal structures, along with their estimated standard deviations, are presented in Tables 2 and 3 and selected bond lengths and angles are presented in Tables 4 and 5.

Additional material available from the Cambridge Crystallo-

Table 2 Atomic coordinates ($\times 10^5$ for Cd, $\times 10^4$ for other atoms) for complexes **1** and **2**

	Complex **1**				Complex **2**		
Atom	*x*	*y*	*z*		*x*	*y*	*z*
Cd(1)	17 820(6)	8 260(5)	50 109(3)		17 777(9)	8 094(5)	49 999(3)
P(1)	2 164(2)	−3 535(2)	2 497(1)		2 068(3)	−3 739(2)	2 603(1)
C(1)	2 058(12)	−4 721(8)	3 557(5)		2 133(15)	−4 801(9)	3 632(5)
C(2)	2 027(14)	−5 661(10)	3 795(6)		2 137(19)	−5 740(12)	3 865(7)
C(3)	2 013(12)	−6 632(9)	3 326(7)		1 958(16)	−6 761(10)	3 417(7)
C(4)	1 970(11)	−6 687(8)	2 620(6)		1 784(14)	−6 877(8)	2 716(7)
C(5)	2 012(10)	−5 744(8)	2 365(5)		1 799(14)	−5 979(8)	2 458(5)
C(6)	2 034(9)	−4 762(7)	2 828(4)		1 968(11)	−4 914(7)	2 932(4)
C(7)	−709(10)	−4 868(8)	1 565(5)		−865(15)	−5 092(9)	1 730(6)
C(8)	−1 887(12)	−5 123(10)	966(6)		−2 054(16)	−5 392(10)	1 134(7)
C(9)	−1 743(13)	−4 405(11)	526(5)		−1 858(20)	−4 772(14)	670(6)
C(10)	−460(13)	−3 432(10)	680(5)		−552(17)	−3 817(14)	793(7)
C(11)	706(11)	−3 169(8)	1 271(5)		632(15)	−3 520(10)	1 393(6)
C(12)	604(9)	−3 896(7)	1 722(4)		483(12)	−4 152(7)	1 850(4)
C(13)	4 061(10)	−3 540(8)	1 490(4)		3 996(13)	−3 837(8)	1 644(4)
C(14)	5 477(12)	−3 245(9)	1 272(5)		5 405(14)	−3 561(9)	1 447(6)
C(15)	6 817(12)	−2 498(9)	1 750(6)		6 717(15)	−2 765(9)	1 900(6)
C(16)	6 741(10)	−2 031(8)	2 455(5)		6 649(14)	−2 230(9)	2 571(6)
C(17)	5 328(10)	−2 328(7)	2 670(4)		5 259(13)	−2 485(8)	2 804(5)
C(18)	3 986(9)	−3 086(6)	2 193(4)		3 897(11)	−3 314(7)	2 321(4)
C(19)	2 031(9)	−2 407(7)	3 190(4)		1 982(12)	−2 553(7)	3 274(4)
C(20)	417(10)	−2 641(8)	3 378(4)		370(13)	−2 781(8)	3 458(5)
C(21)	268(13)	−1 686(9)	3 954(5)		237(16)	−1 760(9)	4 013(5)
O(1)	1 404(9)	−781(6)	4 151(3)		1 353(11)	−857(6)	4 184(4)
O(2)	−1 012(8)	−1 909(6)	4 159(3)		−1 041(10)	−1 986(6)	4 208(4)
P(2)	4 344(2)	−1 539(2)	7 460(1)		4 478(3)	−1 338(2)	7 400(1)
C(22)	3 541(11)	−3 572(7)	6 417(5)		3 493(15)	−3 439(9)	6 370(5)
C(23)	3 321(13)	−4 729(9)	6 181(5)		3 216(18)	−4 609(9)	6 134(6)
C(24)	3 522(12)	−5 326(8)	6 674(6)		3 541(15)	−5 167(9)	6 591(7)
C(25)	3 921(11)	−4 802(8)	7 401(5)		4 087(14)	−4 578(9)	7 286(7)
C(26)	4 130(10)	−3 649(7)	7 648(4)		4 351(14)	−3 427(8)	7 541(5)
C(27)	3 937(8)	−3 027(6)	7 148(4)		4 041(12)	−2 861(7)	7 067(5)
C(28)	2 206(10)	−2 045(8)	8 349(5)		2 428(14)	−1 813(9)	8 271(5)
C(29)	1 567(12)	−1 777(10)	8 960(6)		1 807(16)	−1 540(11)	8 866(6)
C(30)	2 195(14)	−721(12)	9 427(5)		2 473(19)	−444(14)	9 327(6)
C(31)	3 431(12)	110(10)	9 308(5)		3 663(17)	384(12)	9 204(7)
C(32)	4 076(11)	−142(8)	8 708(5)		4 244(15)	102(9)	8 605(6)
C(33)	3 477(9)	−1 229(7)	8 233(4)		3 641(12)	−1 010(8)	8 148(4)
C(34)	7 179(9)	−739(7)	8 448(4)		7 355(15)	−490(8)	8 355(5)
C(35)	8 809(10)	−290(8)	8 643(5)		8 969(15)	−9(9)	8 557(5)
C(36)	9 696(10)	59(8)	8 149(5)		9 836(15)	331(9)	8 088(6)
C(37)	8 943(10)	−47(7)	7 449(5)		9 076(14)	190(9)	7 422(6)
C(38)	7 347(9)	−474(7)	7 250(4)		7 460(13)	−287(8)	7 204(5)
C(39)	6 435(9)	−837(6)	7 741(4)		6 584(11)	−624(7)	7 683(5)
C(40)	3 606(9)	−994(7)	6 758(4)		3 710(12)	−821(8)	6 729(4)
C(41)	1 833(9)	−1 435(8)	6 542(4)		1 903(13)	−1 249(9)	6 539(5)
C(42)	1 183(13)	−899(9)	6 010(4)		1 242(17)	−770(9)	6 000(5)
O(3)	2 137(8)	−122(5)	5 832(3)		2 187(10)	−33(6)	5 806(3)
O(4)	−281(8)	−1 301(6)	5 783(3)		−229(11)	−1 177(7)	5 794(4)
N(1)	4 947(8)	2 033(6)	5 029(4)		4 970(12)	2 014(7)	5 006(5)
O(5)	4 479(8)	2 016(8)	5 585(4)		4 482(11)	2 062(9)	5 538(4)
O(6)	3 952(8)	−1 598(8)	4 477(3)		3 937(12)	1 515(10)	4 465(4)
O(7)	6 363(7)	2 468(6)	5 023(3)		6 353(10)	2 449(7)	4 997(4)
N(2)	3 243(17)	2 788(11)	566(5)	Cl(1)	2 729(5)	2 729(3)	459(1)
O(8)	4 429(11)	2 533(7)	554(4)	O(8)	3 857(19)	3 604(14)	287(10)
O(10)	3 307(19)	3 715(11)	822(5)	O(9)	1 828(21)	1 984(14)	−177(8)
O(9)	1 970(12)	2 046(12)	296(7)	O(10)	1 697(18)	3 393(12)	713(8)
				O(11)	3 232(32)	2 413(22)	962(11)
				O(8′)	4 008(16)	2 306(13)	705(8)
				O(9′)	1 419(18)	1 695(14)	317(11)
				O(10′)	2 789(34)	3 559(17)	974(11)
				O(11′)	2 982(23)	2 823(16)	−175(7)

graphic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Infrared Spectroscopy.—The co-ordination of a carboxylate group to Cd^{II} causes a red shift of both asymmetric and symmetric stretching frequencies. The difference between the asymmetric and symmetric stretching of a carboxylate group is commonly used to estimate its co-ordination mode to metal ions.[25–27] For ligand L and **1**, **2** and **3**, $\Delta\nu = \nu_{asym} - \nu_{sym}$ are 214, 249, 250 and 253 cm^{-1}, respectively. As there is no significant difference between the latter three values, the bridging mode of the carboxylate group with metal ions does not change the symmetry of the group significantly.

Table 3 Atomic coordinates (× 10^5 for Cd, × 10^4 for other atoms) for complex **3**

Atom	*x*	*y*	*z*
Cd(1)	58 780(6)	50 000	90 907(9)
Cl(1)	7 225(4)	5 000	7 904(8)
P(1)	2 464(2)	3 814(1)	4 109(3)
C(1)	883(9)	4 348(3)	3 023(18)
C(2)	−127(13)	4 476(4)	2 175(27)
C(3)	−956(10)	4 243(4)	1 322(16)
C(4)	−745(8)	3 887(4)	1 364(12)
C(5)	277(8)	3 755(3)	2 236(11)
C(6)	1 104(7)	3 989(2)	3 088(10)
C(7)	1 544(9)	3 374(3)	5 705(12)
C(8)	1 566(10)	3 068(3)	6 615(14)
C(9)	2 407(12)	2 831(3)	7 059(13)
C(10)	3 309(12)	2 900(3)	6 658(15)
C(11)	3 299(9)	3 192(3)	5 736(12)
C(12)	2 421(7)	3 432(2)	5 248(10)
C(13)	2 842(8)	3 326(3)	2 141(11)
C(14)	3 216(9)	3 212(3)	991(12)
C(15)	3 764(8)	3 461(3)	450(12)
C(16)	3 927(9)	3 804(3)	1 027(12)
C(17)	3 571(7)	3 909(3)	2 147(11)
C(18)	3 027(6)	3 666(2)	2 715(9)
C(19)	3 335(7)	4 155(3)	5 368(10)
C(20)	3 038(9)	4 237(3)	6 765(12)
C(21)	3 807(8)	4 495(2)	7 927(11)
O(1)	4 640(5)	4 592(2)	7 692(8)
O(2)	3 507(6)	4 599(2)	8 985(8)
Cl(2)	5 000	2 264(1)	0
O(5)	5 750(13)	2 529(6)	−183(31)
O(6)	4 445(17)	2 142(6)	−1 584(18)
O(5′)	4 829(35)	2 047(9)	−1 265(15)
O(6′)	3 996(16)	2 292(8)	184(34)

Description of the Structures.—The discrete centrosymmetric dimeric cation $[\{Cd[Ph_3P(CH_2)_2CO_2]_2(NO_3)\}_2]^{2+}$ of complex **1** is shown in Fig. 1. In this dinuclear species, four $Ph_3P(CH_2)_2CO_2$ ligands lying ≈90° apart about the Cd ··· Cd direction bridge the metal centres in a *syn–syn* manner. The apical sites at both terminals of the Cd ··· Cd axis are each occupied by a chelating NO_3^- ligand, and the angle between the plane O(5)–N(1)–O(6) and the plane O(1)–C(21)–O(2) is 48.4°. To our knowledge, this is the only example of this kind of complex which has the apical site occupied by a chelating ligand. The Cd(1) ··· Cd(1a) separation is 3.278(2) Å, which indicates that there is no significant interaction between the metal atoms (the interatomic distance in metallic cadmium is 3.04 Å).[28] The co-ordination geometry about the cadmium ion

Table 5 Bond lengths (Å) and angles (°) for complex **3**

Cd(1)–Cl(1)	2.432(8)	Cd(1)–O(1)	2.251(6)
Cd(1) ··· Cd(1a)	3.361(2)	Cd(1)–O(1a)	2.251(6)
Cd(1)–O(2a)	2.236(7)	Cd(1)–O(2b)	2.236(7)
C(19)–C(20)	1.527(17)	C(20)–C(21)	1.514(13)
C(21)–O(1)	1.257(14)	C(21)–O(2)	1.255(14)
O(2)–Cd(1a)	2.236(7)		
Cl(1)–Cd(1)–O(1)	103.7(2)	Cl(1)–Cd(1)–Cd(1c)	177.1(1)
O(1)–Cd(1)–Cd(1a)	78.4(2)	Cl(1)–Cd(1)–O(1a)	103.7(2)
O(1)–Cd(1)–O(1a)	84.9(3)	Cd(1c)–Cd(1)–O(1a)	78.4(2)
Cl(1)–Cd(1)–O(2a)	105.0(3)	O(1)–Cd(1)–O(2a)	151.3(3)
Cd(1c)–Cd(1)–O(2a)	73.0(2)	O(1a)–Cd(1)–O(2a)	88.5(2)
Cl(1)–Cd(1)–O(2b)	105.0(3)	O(1)–Cd(1)–O(2b)	88.5(2)
Cd(1c)–Cd(1)–O(2b)	73.0(2)	O(1a)–Cd(1)–O(2b)	151.3(3)
O(2a)–Cd(1)–O(2b)	84.0(4)	Cd(1)–O(1)–C(21)	126.0(6)
C(21)–O(2)–Cd(1c)	135.0(7)	C(19)–C(20)–C(21)	114.5(10)
C(20)–C(21)–O(1)	117.0(10)	C(20)–C(21)–O(2)	115.3(10)
O(1)–C(21)–O(2)	127.6(8)		

Symmetry transformations: a *x*, 1 − *y*, *z*; b 1 − *x*, 1 − *y*, 2 − *z*; c 1 − *x*, *y*, 2 − *z*.

Table 4 Bond lengths (Å) and angles (°) for complexes **1** and **2**

	1	**2**		**1**	**2**
Cd(1)–O(1)	2.254(7)	2.240(7)	Cd(1)–O(3)	2.242(8)	2.220(8)
Cd(1)–O(5)	2.428(7)	2.426(8)	Cd(1)–O(6)	2.389(8)	2.409(10)
Cd(1) ··· Cd(1a)	3.278(2)	3.278(2)	Cd(1)–O(2a)	2.223(7)	2.231(9)
Cd(1)–O(4a)	2.235(8)	2.235(10)	C(19)–C(20)	1.520(13)	1.523(16)
C(20)–C(21)	1.523(14)	1.546(16)	C(21)–O(1)	1.238(11)	1.223(13)
C(21)–O(2)	1.250(13)	1.252(16)	C(40)–C(41)	1.511(11)	1.534(15)
C(41)–C(42)	1.512(15)	1.524(18)	C(42)–O(3)	1.244(12)	1.253(14)
C(42)–O(4)	1.256(13)	1.253(16)	N(1)–O(5)	1.206(11)	1.205(14)
N(1)–O(6)	1.208(9)	1.228(11)	N(1)–O(7)	1.244(9)	1.220(14)
O(1)–Cd(1)–O(3)	87.1(3)	87.3(3)	O(1)–Cd(1)–O(5)	117.2(3)	118.3(4)
O(3)–Cd(1)–O(5)	82.4(3)	83.1(3)	O(1)–Cd(1)–O(6)	83.3(3)	83.6(3)
O(3)–Cd(1)–O(6)	117.7(3)	117.4(4)	O(5)–Cd(1)–O(6)	50.2(2)	49.9(3)
O(1)–Cd(1)–Cd(1a)	75.9(2)	75.6(2)	O(3)–Cd(1)–Cd(1a)	76.0(2)	76.3(2)
O(5)–Cd(1)–Cd(1a)	154.3(2)	154.8(2)	O(6)–Cd(1)–Cd(1a)	154.7(2)	154.7(2)
O(1)–Cd(1)–O(2a)	153.1(3)	153.0(3)	O(3)–Cd(1)–O(2a)	87.4(3)	88.1(3)
O(5)–Cd(1)–O(2a)	88.1(3)	87.5(3)	O(6)–Cd(1)–O(2a)	122.0(3)	121.8(3)
Cd(1a)–Cd(1)–O(2a)	77.2(2)	77.5(2)	O(1)–Cd(1)–O(4a)	88.5(3)	87.3(3)
O(3)–Cd(1)–O(4a)	152.9(2)	153.0(3)	O(5)–Cd(1)–O(4a)	123.0(3)	122.4(4)
O(6)–Cd(1)–O(4a)	88.3(3)	88.2(4)	Cd(1a)–Cd(1)–O(4a)	77.0(2)	76.7(2)
O(2a)–Cd(1)–O(4a)	84.5(3)	84.8(3)	C(19)–C(20)–C(21)	115.0(7)	114.2(8)
C(20)–C(21)–O(1)	116.6(10)	116.6(12)	C(20)–C(21)–O(2)	115.4(8)	113.7(9)
O(1)–C(21)–O(2)	128.0(10)	129.6(11)	Cd(1)–O(1)–C(21)	129.6(7)	129.9(9)
C(21)–O(2)–Cd(1a)	129.1(6)	127.2(6)	C(40)–C(41)–C(42)	114.3(8)	113.6(10)
C(41)–C(42)–O(3)	117.6(9)	118.4(11)	C(41)–C(42)–O(4)	115.8(9)	114.8(10)
O(3)–C(42)–O(4)	126.6(10)	126.8(12)	Cd(1)–O(3)–C(42)	130.8(7)	130.7(8)
C(42)–O(4)–Cd(1a)	129.5(7)	129.4(8)	O(5)–N(1)–O(6)	115.8(7)	113.9(10)
O(5)–N(1)–O(7)	122.2(7)	123.9(9)	O(6)–N(1)–O(7)	122.1(8)	122.2(10)
Cd(1)–O(5)–N(1)	95.8(4)	97.7(6)	Cd(1)–O(6)–N(1)	97.7(6)	97.8(7)

Symmetry transformation: a −*x*, −*y*, −*z*.

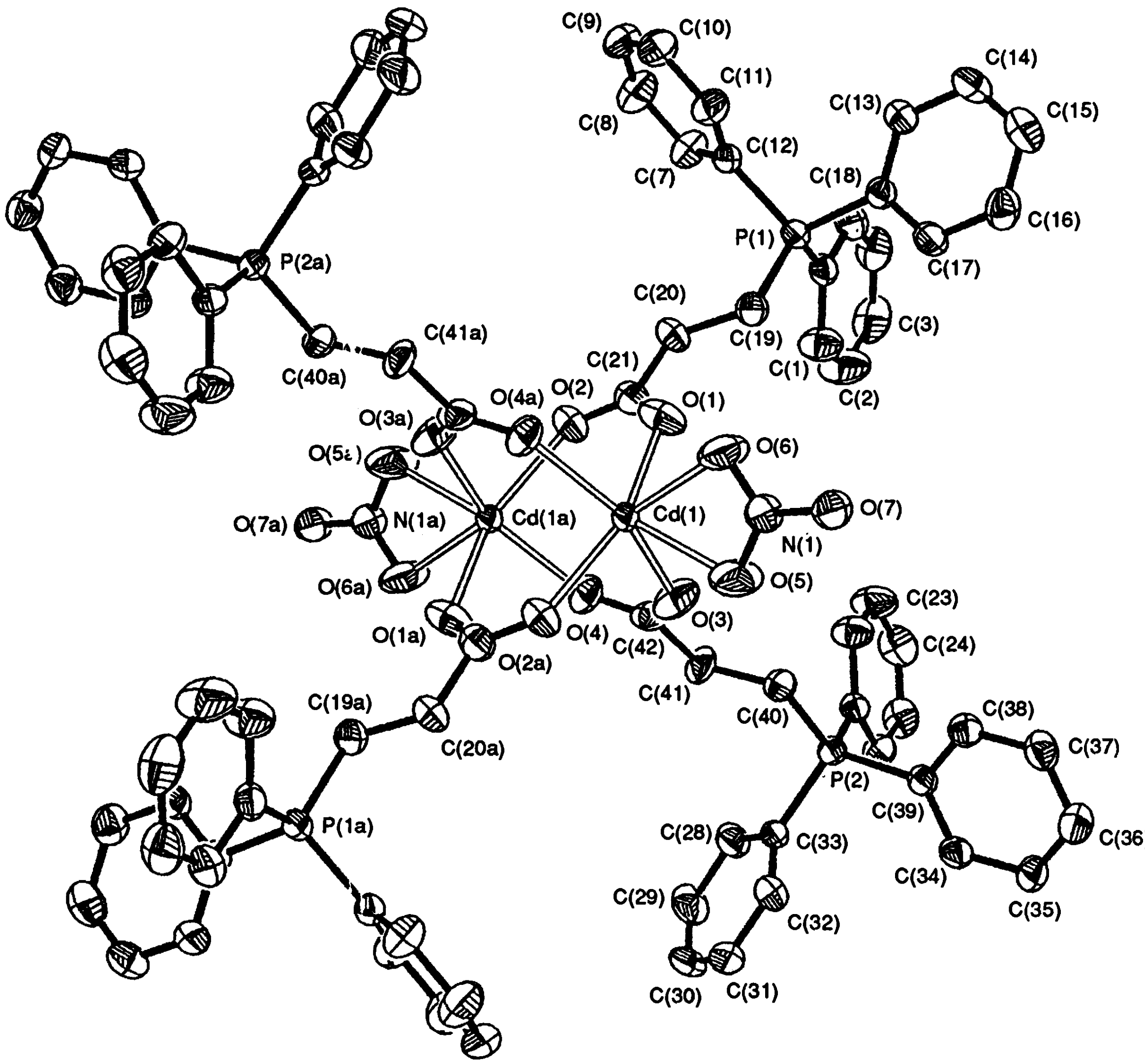

Fig. 1 Molecular structure and atom numbering of the $[\{CdL_2(NO_3)\}_2]^{2+}$ cation in complex **1**. The thermal ellipsoids are drawn at the 35% probability level

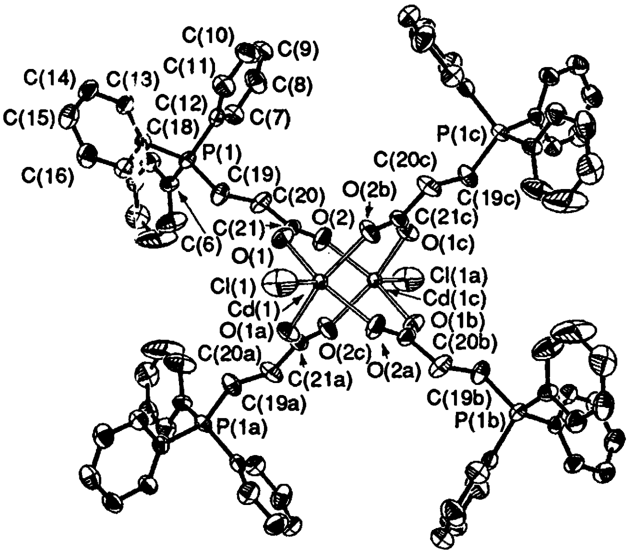

Fig. 2 Molecular structure and atom numbering of the $[(CdL_2Cl)_2]^{2+}$ cation in complex **3**. The thermal ellipsoids are drawn at the 35% probability level

is best described as a distorted CdO_6 octahedron with Cd–O(carboxylate) distances lying between 2.223 and 2.255 Å, and the C–O–Cd angles in the range 129.1–130.8°, the most distorted angle being O(5)–Cd(1)–O(6) at 50.2(2)°. The tetrakis(μ-carboxylato) dimetal skeleton of this compound conforms closely to idealized D_{4h} symmetry as both carboxylate oxygen atoms of each ligand L are symmetrically co-ordinated to the metals. The angle Cd(la)–Cd(1)–N(1) is 173.6°, so the metal atoms lie approximately on a C_2 symmetry axis. This is different from that of the structure of $[\{Cd(CF_3CO_2)_2(PPh_3)\}_2]$ in which one of the carboxylato groups is seriously distorted. The Cd–O(nitrato) distances of 2.389(8) and 2.428(7) Å are significantly shorter than those [2.542(5) and 2.488(6) Å] in $Cd(OH)(NO_3)$.[29]

Complex **2** is isomorphous with complex **1**, and changing the counter anion from nitrate to perchlorate has no appreciable effect on the structure of the tetrakis(μ-carboxylato) dimetal dication (Table 4). The non-bonded Cd(1) ··· Cd(1a) distance is 3.278(2) Å.

The cation of complex **3** has a tetrakis(μ-carboxylato)-bridged dimetal framework lying on a site of symmetry 2/*m*, but the apical site at each terminal of the Cd ··· Cd axis is now occupied by a chloride anion (Fig. 2). The non-bonded Cd(1) ··· Cd(1a) distance in the unit $[\{Cd[Ph_3P(CH_2)_2CO_2]_2Cl\}_2]^{2+}$ is 3.361(2) Å. The cadmium ion is five-co-ordinated in a CdO_4Cl square pyramid. The Cd–O distances are 2.236(7) and 2.251(6) Å, and the Cd–Cl distance is 2.432(8) Å. In comparison with

$[\{Cd[Ph_3P(CH_2)_2CO_2]_2(NO_3)\}_2]^{2+}$, the structure of $[\{Cd[Ph_3P(CH_2)_2CO_2]_2Cl\}_2]^{2+}$ is significantly distorted, the difference between angles Cd(1)–O(1)–C(21) and Cd(lc)–O(2)–C(21) being 9°. In all three complexes **1**–**3**, the geometry of the triphenylphosphine moiety is normal.

With a delocalized π system and a pair of lone-pair electrons on the oxygen atoms, the carboxylate group, as one of the common triatomic bridging ligands, is of special importance for multiply bonded M–M systems. The effects of different carboxylate and axial ligands on the M–M distance have been extensively discussed, especially for Cr–Cr multiple bonds.[20,21,30] It has been concluded that the M–M distance depends not only on the nature of the bridging carboxylate moiety, but also on the co-ordination strength of the axial ligands: the more basic the carboxylic acid anion, the shorter the M–M distance and the stronger the axial ligand, the longer the M–M distance.

According to the Pearson acid–base theory,[31] bonds will normally form only when the Lewis-acid strength of the electron acceptor is *close* to the Lewis-base strength of the electron donor. When the difference between the acid strength and base strength is large, the ligand will be deformed to adjust its base strength in order to match the acid strength of the metal. On the other hand, the co-ordination of a ligand to a metal centre will change the acid strength of the metal ion, such that it will be reduced if the base strength of the ligand is high, and *vice versa*. So it can be generalized that the softer the axial ligand and the weaker the base strength of the carboxylate group, the more distorted the carboxylate group becomes.

In view of the induction effect of the Ph_3P^+ moiety, it can be expected that the base strength of the ligand L lies between those of acetic acid and trifluoroacetic acid (C–O bond lengths and O–C–O bond angles are 1.26, 124 and 1.24 Å, 128°, respectively).[32] On the other hand, according to the Pearson acid–base classification, cadmium(II) is a soft acid and the hardness of Cl, O and P varies in the order $O > Cl > P$.[31] In all three complexes **1**–**3** the $Cd\cdots Cd$ distance is significantly shorter than that of 3.452(1) Å in $[\{Cd(CF_3CO_2)_2(PPh_3)\}_2]$ (0.174, 0.174 and 0.091 Å shorter, respectively), which is similar to the result obtained from analogous chromium(II) carboxylate complexes.[30] In complexes **1** and **2**, the tetrakis(μ-carboxylato) dimetal frame has a high symmetry, but for complex **3** the carboxylate group is significantly distorted [the difference between angles Cd(1)–O(1)–C(21) and Cd(1c)–O(2)–C(21) is 9°], although to a much lesser extent than in $[\{Cd(CF_3CO_2)_2(PPh_3)\}_2]$ (4.6 and 45.2°, respectively). It is obvious that besides the steric interaction between the bulky axial ligand and carboxylate group, there is a significant electronic interaction which accounts for the observed distortion.

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