914 *Inorg. Chem.* **1984**, *23*, 914–918

$2n + 1$, indicated the space group $P2_1/c$.

Solution and Refinement of the Crystal Structure. The structure was solved by heavy-atom methods and refined to $R \approx 0.16$, with anisotropic temperature factors, with no problems. At this point a difference map showed further peaks, which were taken to be an EtOH of solution. C(48) also showed evidence of disorder, occupying two positions. These were included at 0.5 occupancy and refined isotropically. Further refinement led to convergence at $R = 0.083$, $R_w = 0.107$. Although the PF_6 anions and the EtOH showed evidence of disorder (large temperature factors), no alternative atomic positions could be discerned on a difference map. Those hydrogen atoms whose positions are completely defined were included at fixed positions and not refined; other hydrogen atoms were omitted.

Final refinement was by least squares in large blocks. An empirical weighting scheme of the form $w = 1/(1.0 + ((F - B)/A)^2)$ was used, where A was taken as 60.0 and B as 25.0. This was shown to be satisfactory by a weight analysis. Computing was with the X-RAY 76 system[20] on Burroughs B6700 and CDC 7600 computers. Scattering factors in the analytical form and anomalous dispersion factors (for Ni and P) were taken from ref 21. Final solution details are in Table VIII, final atomic coordinates are in Table IX, and a listing of anisotropic temperature factors and observed and calculated structure factors are listed as supplementary material.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged. We are also grateful to Dr. R. Thomas of Hobart University, Tasmania, Australia, for his gift of the α,α'-bis(methylamino)-*m*-xylene and T. Meade for assistance in obtaining ^{13}C NMR spectra at high field.

Registry No. I (R^1 = *m* = xylylene, $R^2 = CH_3$, R^3 = H), 88635-25-0; I (R^1 = *m*-xylylene, $R^2 = CH_3$, R^3 = 3,5-$(OMe)_2Ph$), 88635-27-2; I (R^1 = *m*-xylylene, $R^2 = CH_3$, R^3 = *n*-C_7H_{15}), 88635-29-4; I (R^1 = *m*-xylylene, $R^2 = CH_3$, $R^3 = C_6H_5$), 88635-31-8; I (R^1 = *m*-xylylene, R^2 = H, $R^3 = C_6H_5$), 88635-33-0; I (R^1 = *m*-xylylene, R^2 = H, R^3 = *n*-C_7H_{15}), 88635-35-2; I (R^1 = *m*-xylylene, $R^2 = CH_2C_6H_5$, $R^3 = C_6H_5$), 88635-37-4; I ($R^1 = (CH_2)_4$, R^2 = H, $R^3 = C_6H_5$), 88635-39-6; I ($R^1 = (CH_2)_4$, $R^2 = CH_3$, $R^3 = C_6H_5$), 88610-65-5; I ($R^1 = (CH_2)_4$, R^2 = H, R^3 = *t*-C_4H_9), 88610-67-7; I ($R^1 = (CH_2)_5$, R^2 = H, $R^3 = C_6H_5$), 88610-69-9; I ($R^1 = (CH_2)_5$, $R^2 = CH_3$, $R^3 = C_6H_5$), 88610-71-3; I ($R^1 = (CH_2)_5$, R^2 = H, R^3 = *t*-C_4H_9), 88610-73-5; I ($R^1 = (CH_2)_6$, R^2 = H, $R^3 = C_6H_5$), 88610-75-7; I ($R^1 = (CH_2)_6$, $R^2 = CH_3$, $R^3 = C_6H_5$), 88610-77-9; I ($R^1 = (CH_2)_6$, R^2 = H, R^3 = *t*-C_4H_9), 88610-79-1; I ($R^1 = (CH_2)_6$, R^2 = H, R^3 = *n*-C_7H_{15}), 88635-15-8; I ($R^1 = (CH_2)_6$, $R^2 = CH_3$, R^3 = H), 88610-81-5; I ($R^1 = (CH_2)_7$, R^2 = H, $R^3 = C_6H_5$), 88610-83-7; I ($R^1 = (CH_2)_7$, $R^2 = CH_3$, $R^3 = C_6H_5$), 88610-85-9; I ($R^1 = (CH_2)_7$, R^2 = H, R^3 = *t*-C_4H_9), 88610-87-1; I ($R^1 = (CH_2)_8$, R^2 = H, $R^3 = C_6H_5$), 88610-89-3; I (R^1 = *m*-xylylene, $R^2 = CH_3$, $R^3 = CH_3$), 77827-37-3; I (R^1 = *m*-xylylene, R^2 = H, $R^3 = CH_3$), 77827-31-7; I (R^1 = *m*-xylylene, $R^2 = CH_2C_6H_5$, $R^3 = CH_3$), 77827-39-5; IV, 74466-59-4; V (R^3 = H), 88611-06-7; V (R^3 = *t*-C_4H_9), 88611-07-8; V (R^3 = *neo*-C_5H_{11}), 88611-08-9; V (R^3 = *n*-C_7H_{15}), 88610-90-6; V (R^3 = *n*-C_9H_{19}), 88611-09-0; V ($R^3 = C_6H_5$), 74466-43-6; V ($R^3 = CH_2C_6H_5$), 88611-10-3; V ($R^3 = CF_3$), 88611-11-4; V (R^3 = 4-OMePh), 88611-12-5; V (R^3 = 3,5-$(OMe)_2Ph$), 88611-13-6; V (R^3 = 3,5-Me_2Ph), 88611-14-7; V (R^3 = 3,5-$(NO_2)_2Ph$), 88611-15-8; V (R^3 = *n*-C_5H_{11}), 88611-16-9; V (R^3 = *n*-$C_{17}H_{35}$), 88611-17-0; V ($R^3 = C_6F_5$), 88610-91-7; VI (R^3 = H), 88610-93-9; VI (R^3 = *t*-C_4H_9), 88610-95-1; VI (R^3 = *n*-C_7H_{15}), 88610-97-3; VI ($R^3 = C_6H_5$), 88610-99-5; VI ($R^3 = CF_3$), 88611-01-2; VI (R^3 = *neo*-C_5H_{11}), 88611-03-4; VII ($R^2 = CH_3$, $R^3 = C_6F_5$), 88635-17-0; VII ($R^2 = CH_3$, R^3 = *p*-biphenyl), 88635-19-2; VII ($R^2 = CH_3$, R^3 = *p*-ClPh), 88635-21-6; VII ($R^2 = CH_3$, R^3 = *p*-FPh), 88635-23-8; VII ($R^2 = CH_2C_6H_5$, $R^3 = C_6H_5$), 88611-05-6; formic acid, 64-18-6; acetic anhydride, 108-24-7; trimethylacetyl chloride, 3282-30-2; perfluoroacetyl chloride, 354-32-5; benzylamine, 100-46-9; α,α'-dibromo-*m*-xylene, 626-15-3; α,α'-bis(methylamino)-*m*-xylene, 23399-62-4; α,α'-bis(methylamino)-*m*-xylene (formamide derivative), 59276-03-8; α,α'-diamino-*m*-xylene, 1477-55-0.

Supplementary Material Available: Listings of anisotropic temperature factors and observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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Crystal Structure of Tetrakis(μ-trifluoroacetato)bis[(triphenylphosphine)cadmium(II)]: A Dimer Containing the Tetrakis(carboxylato)dimetal Framework

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The title compound belongs to the monoclinic space group $P2_1/c$, with a = 10.011 (7) Å, b = 18.062 (5) Å, c = 15.135 (4) Å, β = 118.34 (4)°, and Z = 2 $[Cd(CF_3COO)_2P(C_6H_5)_3]_2$ molecules per cell. The structure was solved on 1741 observed reflections to an R factor of 0.038. The unit cell contains discrete centrosymmetric dimeric molecules in which the Cd atoms are part of a framework of four bridging carboxylate ligands, similar to those found with Mo(II), Cu(II), Cr(II), and Rh(II). The apical sites are occupied by PPh_3 ligands (Cd–P = 2.524 Å), but the Cd–P bond does not lie along the Cd–Cd axis (Cd–Cd–P = 153.7°). The Cd–Cd separation (3.452 Å) is consistent with the absence of metal–metal bonding. One pair of carboxylate groups is symmetrically coordinated (Cd–O–C = 128.2 and 132.8°) as usually found in tetrakis(μ-carboxylate) frameworks, but the other pair undergoes considerable distortion (Cd–O–C = 109.0 and 154.2°).

Introduction

Our knowledge of tertiary phosphine complexes of cadmium has, until recently, been limited to the complexes of cadmium(II) halides,[2,3] which were first reported[2] in 1940. Complexes of cadmium(II) thiocyanate with tri-*tert*-butyl-,[4] tri-

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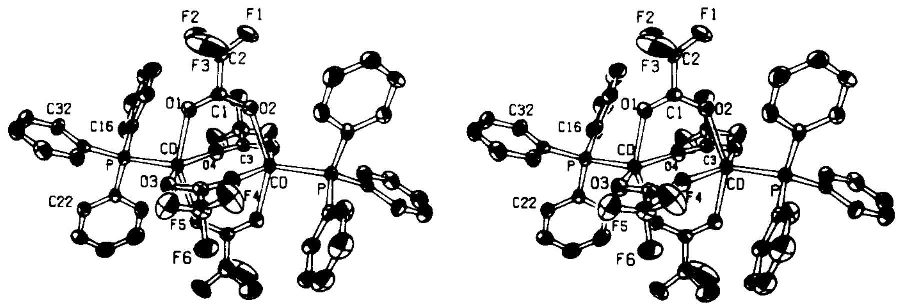

Figure 1. Stereoview of the $[Cd(CF_3COO)_2PPh_3]_2$ molecule. The ellipsoids correspond to 35% probability. The phenyl carbon atoms are assigned two-digit symbols: the first digit identifies the ring; the second indicates the position in the ring, position 1 corresponding to the carbon attached to P. The hydrogens are omitted.

cyclohexyl-,[5] triphenyl-,[5] and tri-*m*-tolylphosphines[5] have been prepared very recently; the structure of $Cd(SCN)_2P(m\text{-tol})_3$ has also been determined by a single-crystal X-ray diffraction study. In a subsequent study,[6] triphenylphosphine complexes of cadmium(II) perchlorate, nitrate, and trifluoroacetate have been prepared and characterized by spectroscopic measurements.

Cadmium(II) trifluoroacetate forms isolable 1:1 as well as 1:2 complexes with triphenylphosphine. Although both the complexes are indicated to be nonionic compounds, it proved difficult to ascertain their structural features by vibrational and ^{31}P and ^{19}F NMR spectral measurements. Carboxylate groups can act as either unidentate or bidentate ligands, and in the latter case, they may form chelates and/or bridges often leading to complicated polymeric patterns in the solids.[7] The infrared spectra of the two Cd complexes showed very similar bands (at ca. 1650 and 1690 cm^{-1}) due to the antisymmetric CO_2 stretching modes of the coordinated trifluoroacetato groups. It was difficult to assign the symmetric CO_2 stretching frequency due to the presence of several other ligand bands in this region. The ^{19}F NMR spectra of both complexes are almost identical and exhibit a single resonance (at ca. δ 74.15 upfield of $CFCl_3$). Although their $^1J(Cd\text{–}P)$ values are markedly different, they do not provide information pertaining to the coordination around cadmium in either complex. In view of the scarcity of structural data on metal trifluoroacetato compounds, a single-crystal X-ray diffraction study was undertaken on the 1:1 cadmium(II) complex.

The structures of a number of simple cadmium carboxylates have been determined,[8] and they invariably show intricate three-dimensional arrangements of carboxylate groups bridging Cd atoms. Surprisingly, the present compound was found to contain discrete units in which two metal atoms are brought together by four bridging carboxylate groups, in a pattern common for Cu(II), Mo(II), Cr(II), and Rh(II), but never reported so far for Cd(II).

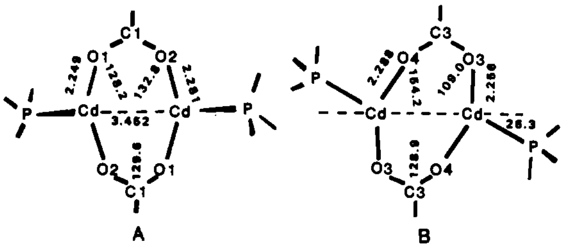

Figure 2. Two projections of the bridging framework ~90° apart about the Cd–Cd axis.

Experimental Section

Crystal Data: $C_{44}H_{30}Cd_2F_{12}O_8P_2$; fw 1201.5; monoclinic; space group $P2_1/c$; $a = 10.011$ (7), $b = 18.062$ (5), $c = 15.135$ (4) Å; $\beta = 118.34$ (4)°; $V = 2408.7$ Å^3; $Z = 2$ dimers per cell; $D_{calcd} = 1.656$ g cm^{-3}; λ(Mo K$\bar{\alpha}$) = 0.71067 Å (graphite monochromator); $T = 22$ °C; μ(Mo Kα) = 10.4 cm^{-1}; crystal dimensions 0.30 × 0.30 × 0.05 mm.

Crystallographic Measurements. Colorless plates were obtained as described elsewhere.[6] The crystal was mounted on an Enraf-Nonius CAD4 diffractometer, and a set of 25 reflections were obtained by the SEARCH procedure of the CAD4 software. These reflections were centered several times, and the indexing routine deduced a reduced cell of monoclinic symmetry. No higher symmetry was suggested by the Niggli parameters. Long-exposure oscillation photographs taken about the crystallographic axes showed the expected layer-line spacings, a Laue mirror was observed for the oscillation about *b*. Fast scans on the 0*k*0 and *h*0*l* reflections indicated that the space group was $P2_1/c$. This was subsequently confirmed by inspection of the complete data set.

The intensity data were collected as described elsewhere.[5] A total of 3148 *hkl* and $hk\bar{l}$ reflections ($2\theta \leq 45°$) were collected (σ on standard intensities =2.6%).

The structure was solved by the conventional heavy-atom method and refined on 1741 nonzero reflections ($I \geq 3\sigma(I)$). The phenyl hydrogens were fixed at ideal positions (C–H = 0.95 Å, $B = 7.0$ Å^2). The hydrogen parameters were not varied, but the coordinates were recalculated after each least-squares cycle. Anisotropic refinement of all non-hydrogen atoms converged to $R = 0.038$ and $R_w = 0.043$. The goodness-of-fit ratio was 1.40. The refined coordinates and equivalent temperature factors are given in Table I. Fluorines in CF_3 groups commonly show high thermal motion. However, one of the CF_3CO_2 ligands has markedly high temperature factors, not only for the fluorines (F1, F2, F3) but also for C2 (Table I). It is likely that, in addition to some rotation of the CF_3 group about the C2-C1 bond, disorder or oscillation involving the (C)–CF_3 unit may take place. The highest peaks in the final ΔF map (± 0.44–0.51 e Å^{-3}) were indeed found near the F atoms involved and Cd. The general background was lower than ±0.26 e Å^{-3}.

The scattering curves were from Cromer and Waber[9] except for hydrogen.[10] The f' and f'' contributions to anomalous dispersion

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Table I. Refined Atomic Coordinates (×10^4; Cd, ×10^5) and Equivalent Temperature Factors (×10^3; Cd and P, ×10^4) of Non-Hydrogen Atoms

atom	x	y	z	U_{eq}, Å^2
Co	5018 (7)	2532 (3)	12178 (4)	557
P	437 (2)	129 (1)	2858 (1)	526
F1	−3754 (7)	1917 (4)	−528 (5)	159
F2	−4143 (11)	1683 (6)	−1866 (6)	265
F3	−5008 (7)	1029 (5)	−1336 (10)	302
F4	2837 (9)	1702 (4)	−699 (6)	163
F5	3433 (7)	2188 (3)	694 (4)	131
F6	1308 (7)	2363 (3)	−518 (5)	122
O1	−2385 (6)	504 (3)	−1373 (4)	74
O2	−1573 (6)	919 (3)	191 (4)	73
O3	1814 (6)	1210 (3)	1052 (4)	74
O4	1088 (6)	731 (3)	−456 (4)	82
C1	−2454 (8)	887 (4)	−717 (6)	54
C2	−3810 (12)	1355 (6)	−1004 (7)	135
C3	1701 (8)	1193 (4)	201 (6)	59
C4	2347 (10)	1857 (5)	−87 (7)	80
C11	268 (8)	−829 (4)	3118 (5)	56
C12	1194 (9)	−1333 (5)	2986 (6)	75
C13	1148 (11)	−2073 (5)	3189 (8)	99
C14	184 (13)	−2326 (5)	3492 (8)	124
C15	−760 (13)	−1846 (6)	3603 (8)	127
C16	−761 (11)	−1094 (5)	3423 (7)	92
C21	−1159 (8)	599 (4)	2859 (5)	55
C22	−1038 (9)	1077 (5)	3598 (6)	74
C23	−2310 (11)	1418 (6)	3560 (7)	102
C24	−3689 (11)	1279 (6)	2776 (8)	108
C25	−3845 (11)	797 (7)	2039 (8)	117
C26	−2573 (10)	466 (5)	2067 (6)	87
C31	2098 (8)	482 (4)	3919 (5)	52
C32	2632 (9)	194 (5)	4887 (6)	79
C33	3886 (11)	511 (6)	5672 (7)	99
C34	4603 (10)	1088 (6)	5518 (7)	101
C35	4139 (10)	1369 (5)	4584 (7)	93
C36	2899 (9)	1054 (5)	3779 (6)	75

Table II. Interatomic Distances and Angles

Distances (Å)			
Cd-P	2.524 (2)	Cd-O3	2.256 (6)
Cd-O1^a	2.249 (6)	Cd-O4^a	2.298 (6)
Cd-O2	2.261 (6)	C1-O1	1.239 (10)
P-C11	1.800 (8)	C1-O2	1.233 (9)
P-C21	1.810 (9)	C3-O3	1.239 (10)
P-C31	1.793 (8)	C3-O4	1.218 (10)
C1-C2	1.479 (15)	C3-C4	1.521 (13)
C2-F1	1.231 (13)	C4-F4	1.268 (14)
C2-F2	1.323 (14)	C4-F5	1.310 (11)
C2-F3	1.211 (16)	C4-F6	1.303 (12)
Cd-Cd	3.452 (1)		
Angles (deg)			
P-Cd-O1^a	104.8 (2)	Cd-Cd-O1^a	75.8 (1)
P-Cd-O2	106.2 (2)	Cd-Cd-O2	72.6 (1)
P-Cd-O3	117.8 (2)	Cd-Cd-O3	88.5 (1)
P-Cd-O4^a	95.2 (2)	Cd-Cd-O4^a	58.5 (1)
O1^a-Cd-O2	147.8 (2)	O1^a-Cd-O3	88.5 (2)
Cd-Cd-P	153.7 (1)	O1^a-Cd-O4^a	85.9 (2)
Cd-P-C11	110.4 (3)	O2-Cd-O3	84.8 (2)
Cd-P-C21	113.2 (3)	O2-Cd-O4^a	82.8 (2)
Cd-P-C31	113.8 (3)	O3-Cd-O4^a	146.9 (2)
C11-P-C21	106.0 (4)	Cd-O1^a-C1^a	128.2 (5)
C11-P-C31	106.8 (4)	Cd-O2-C1	132.8 (5)
C21-P-C31	106.0 (4)	Cd-O3-C3	109.0 (5)
O1-C1-O2	129.6 (8)	Cd-O4^a-C3^a	154.2 (6)
O1-C1-C2	118.5 (8)	O3-C3-O4	128.9 (8)
O2-C1-C2	111.8 (8)	O3-C3-C4	115.9 (7)
C1-C2-F1	121.3 (10)	O4-C3-C4	115.1 (8)
C1-C2-F2	108.2 (9)	C3-C4-F4	113.6 (8)
C1-C2-F3	115.8 (10)	C3-C4-F5	112.6 (8)
F1-C2-F2	97.4 (10)	C3-C4-F6	110.5 (8)
F1-C2-F3	113.9 (11)	F4-C4-F5	108.5 (9)
F2-C2-F3	94.1 (10)	F4-C4-F6	106.4 (9)
		F5-C4-F6	104.8 (8)

^{a} $-x, -y, -z$.

were taken into account for Cd.[11] The programs used are listed elsewhere.[12] The temperature factors, as well as the observed and calculated structure factor amplitudes, are tabulated in the supplementary material.

Description of the Structure

The discrete $[Cd(CF_3COO)_2PPh_3]_2$ centrosymmetric dimer is shown in Figure 1. Four bidentate CF_3COO ligands, lying ~90° apart about the Cd–Cd direction, are bridging the Cd centers in a syn-syn manner. The apical sites at both ends of the Cd–Cd axis are occupied by the PPh_3 molecules.

Tetrakis(μ-carboxylato)dimetal frameworks of this type are known for a number of complexes of Cu(II), Cr(II), Mo(II), Rh(II), and a few other metals.[13,14] These species usually have high symmetry: both carboxylate oxygens are symmetrically coordinated, and no great distortions are produced by the apical ligands even if they are as bulky as PPh_3.[15] In marked contrast, the Cd dimer described here is severely distorted, as can be appreciated from the projections given in Figure 2. Selected interatomic distances and bond angles are listed in Table II. In plane A, the carboxylates are coordinated in the expected manner: the Cd–O distances (2.249 (6) and 2.261 (6) Å) compare well with the short Cd–O bonds involving unidentate oxygen in various cadmium carboxylates.[8] The only anomaly apparent in this plane is the Cd–P bond pointing upward instead of lying in the plane, along the Cd–Cd direction. This is more obvious in projection B at 90° from projection A. This Cd–P bond makes an angle of 26.3° with the Cd–Cd direction. It is slightly shorter (2.524 (2) Å) than in the five-coordinate $Cd(SCN)_2P(m\text{-tol})_3$ complex (2.584 (2) Å).[5] The PPh_3 lone pair lies along the Cd–P direction as usual, as evidenced by the nearly equal Cd–P–Ph angles (110.4, 113.2, and 113.8°; σ = 0.3°). Carboxylate coordination in plane B is very unsymmetrical: the Cd–O4 bond (2.298 (6) Å) is significantly longer than Cd–O3 (2.256 (6) Å), and the CF_3COO groups are so oriented that the Cd–O–C and angles (109.5 (5) and 154.2 (6)°) differ considerably from the value found in ligands A (130.5°).

The geometry of the phosphine is normal. Details on the distances and angles in the phenyl rings are provided in the supplementary material. The C–CF_3 portion of one of the carboxylates is involved in high thermal motion or disorder. Thus, the distances and angles involving C2, F1, F2, and F3 reflect this effect and are unreliable. The geometry of the other carboxylate group is normal.[7]

The packing pattern (Figure 3, supplementary material) shows that the dimers interact by normal van der Waals contacts in the unit cell.

Discussion

The effects on the structure of factors such as the carboxylate "bite", metal–metal bonding, and various features of the apical ligands have been extensively discussed[13] and are still an active research field. With Cr(II), Mo(II), Ru(II), and Rh(II) for instance, the existence of strong M–M bonds is clearly a determining factor.[16,17] In Cu(II) dimers, which also

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Table III

	M-M(complex), Å	M-M(metal),[a] Å	M-O, Å	C-O-M, deg	O-C-O, deg	ref
$[AgCF_3COO]_2$[b]	2.967 (3)	2.88	2.249 (6)	120.7 (5)	130.1 (8)	24
			2.232 (6)	122.3 (5)		
$[CpV(CF_3COO)_2]_2$[c]	3.704	2.70	2.05 (av)	134 (av)	124 (av)	18
$[Pr(CH_3CO_2)_3(H_2O)_3]_2$[c]	4.42	~3.60	2.41 (1)	175 (1)	125 (2)	19
			2.52 (1)	111 (1)		
			2.42 (1)	141 (1)	130 (2)	
			2.45 (1)	141 (1)		
$[Cd(CF_3CO_2)_2PPh_3]_2$	3.452 (1)	3.04	2.249 (6)	128.2 (5)	129.6 (8)	this work
			2.261 (6)	132.8 (5)		
			2.256 (6)	109.0 (5)	128.9 (8)	
			2.298 (6)	154.2 (6)		
$[UO_2(OPPh_3)(CH_3CO_2)_2]_2$[c]	5.582	3.12	2.33 (3)	128 (3)	113 (5)	20
			2.35 (4)	148 (3)		
$[Ni(CH_3CO_2)L]_2$[d]	2.984 (1)	2.50	1.996 (4)	125.8 (3)	125.4 (3)	22
			1.912 (3)	125.6 (3)		
$[Ni(Me_3CCO_2)_2(quinaldine)]_2$[c]	2.754 (3)	2.50	2.04 (1)	124.5 (7)	126 (1)	14
$[Ni(CF_3CO_2)L]_2$[d]	3.151 (2)	2.50	1.904 (7)	130.4 (6)	127.8	21
			1.911 (7)	127.8 (6)		
			1.989 (7)	129.2 (6)	130.3	
			2.038 (8)	124.9 (6)		
$[Ni(CH_3CO_2)L]_2$[d]	3.079 (1)	2.50	1.895 (5)	130.7 (2)	125.8	22
			1.904 (5)	128.4 (2)		
			1.969 (5)	130.3 (2)	126.1	
			2.001 (5)	127.5 (2)		

[a] Reference 23. [b] Bis(μ-carboxylate) (planar). [c] Tetrakis(μ-carboxylate). [d] Bis(μ-carboxylate) (nonplanar); L = 2-(methylallyl)-3-norbornyl.

possess high symmetry, the mechanism of interaction between the Cu atoms is still a debated question.[17] Metal–metal bonding is not prerequisite for the formation of carboxylate-bridged species. Data on systems in which bridging is achieved only by carboxylate groups and M–M bonding is nonexistent or unlikely are given in Table III. Silver trifluoroacetate[24] is unique in being devoid of apical ligands. The Ag–Ag separation is only slightly above the distance in metallic silver. The remaining compounds all contain apical ligands. In all cases, the M–M distance exceeds considerably twice the metallic radius. This suggests that, in the absence of M–M bonding, the bridging framework is quite soft. Distortions are absorbed by this part of the molecule to accommodate steric or electronic requirements of the rest of the metal coordination sphere. For instance, in $[CpV(CF_3CO_2)_2]_2$, where the V–V distance is 3.70 Å, the metal atoms are moved away from each other by the bulky cyclopentadienyl rings in apical positions. In the present case, the PPh_3 ligands probably have a similar effect. The Ph–P–Ph angles here (average 106.3°) are on the average 2–3° greater than in Rh complexes, where the phosphine is more restricted and lies closer to the carboxylate bridge, with the Rh–P bond along the Rh–Rh axis, as a result of metal–metal bonding.

Carboxylate groups can accommodate surprisingly large M–M separations in two ways:[13] by opening the O–C–O angles to ~130° and by retaining appeciable Lewis base character for a wide range of C–O–M angles. Thus, the CF_3COO groups can assemble two molecular fragments in which the metal environment is dictated by its coordination preference and by the steric requirements of the remaining ligands. Factors, other than M–M bonding, leading to carboxylate-bridged dimers instead of monomers with chelated carboxylates are unclear. In fact, for some of the compounds listed in Table III, both bridging and chelating carboxylate groups exist within the same molecule.

In the Cd compound, the two binding modes of bidentate $CF_3CO_2^-$ groups could not be distinguished from the infrared spectra, because the number of observable vibrational modes for the low-symmetry species is not expected to be very sensitive to its environment.[7] Furthermore, the position of the easily recognized OCO antisymmetric stretching band is metal sensitive. Correlation with the frequency difference between the symmetric and the antisymmetric modes seem to be more promising, but in the present case, the symmetric band was masked by phosphine bands. The existence of two components for the antisymmetric vibration (1690 and 1648 cm^{-1}) is consistent with the observed structure. There are two pairs of CF_3COO groups interacting differently with the Cd atoms, and since the bridging framework as a whole is centrosymmetric, only one band is expected to be infrared active for each pair. The low-wavenumber component probably originates in the symmetrically coordinated CF_3COO groups. The other pair of groups, in which one of the oxygens is more weakly bonded to Cd, would behave to some extent as a unidentate carboxylate and, consequently, give rise to the band at 1690 cm^{-1}.

Despite the similar wavenumbers for the OCO stretching bands of the 2:1 $Cd(CF_3CO_2)_2(PPh_3)_2$ complex, the tetrakis(μ-carboxylato) framework is unlikely to be retained, because introducting a second bulky PPh_3 would undoubtedly disrupt the bridging framework. Alternative structures can be put forward, the simplest of which would be a monomer with two chelating carboxylates. Such a model is highly speculative in the absence of further X-ray work on this compound.

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Supplementary Material Available: Listings of refined temperature factors, geometry of the phenyl rings, least-squares planes, calculated coordinates of the hydrogen atoms, and observed and calculated structure factors and a stereoview of the unit cell (Figure 3) (21 pages). Ordering information is given on any current masthead page.

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^{13}C NMR Studies on Diastereotopic Rhodium(III) (±)-2,3-Butanediamine Complexes and the Structure of *lel,lel,lel*-$[Rh((\pm)\text{-bn})_3]Br_3$

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The four possible diastereomers of $[Rh((\pm)\text{-bn})_3]^{3+}$ ("bn" = 2,3-butanediamine, $C_4H_{12}N_2$) have been isolated and the ^{13}C NMR spectra determined. Isomer abundances indicate that the increase in enthalpy per *ob* ring in $[Rh((\pm)\text{-bn})_3]^{3+}$ diastereomers is only one-third that in $[Co((\pm)\text{-bn})_3]^{3+}$ complexes. The *lel,lel,lel* diastereomer of $[Rh((\pm)\text{-bn})_3]^{3+}$ does not exhibit the broadened methyl group ^{13}C NMR resonance found earlier for *lel,lel,lel*-$[Co((\pm)\text{-bn})_3]^{3+}$ even though a crystal structure of the former complex as the bromide salt ($[Rh(C_4H_{12}N_2)_3]Br_3$, trigonal system, space group $P\bar{3}1c$, a = 12.549 (2) Å, c = 8.195 (1) Å, Z = 2) shows a decreased intra-ring methyl group contact distance. These observations rule out steric interactions proposed earlier as a source of the anomalous broadening and indicate that the broadening involves the ^{59}Co atom. ^{13}C NMR spectra of corresponding rhodium(III) and cobalt(III) tris((±)-2,3-butanediamine) diastereomers are virtually identical. The possible contribution of magnetic anisotropy of the metal ion to ^{13}C NMR chemical shift differentiation of diastereotopic carbon atoms in these complexes is discussed.

Introduction

Past studies[1-3] from our group have demonstrated the utility of ^{13}C NMR spectroscopy in differentiating and identifying diastereomeric complexes of diamagnetic metal ions—particularly diastereomers arising from the presence of sinambic[4] ligands. From this work there has arisen an increasingly intriguing question: What is the ultimate origin of ^{13}C NMR chemical shift differences between diastereotopic carbon atoms in such complexes?

Previous work has indicated that, relative to rigid chelates, diastereomers containing flexible chelate rings are more easily differentiated by ^{13}C NMR spectroscopy and that diastereotopic atoms lying in conformationally distinct environments within such complexes have enhanced ^{13}C chemical shift differences.[1,2] Thus, we can readily interpret chemical shift variations between diastereotopic methyl carbon atoms in *ms*-2,3-butanediamine complexes as arising from steric compression shifts[5] associated with axial/equatorial differences in the chelate ring.[1] Moreover, we can explain the striking differentiability of *ms*-2,3-butanediamine diastereomeric complexes as due to the conformational flexibility of the ligand allowing different time-averaged conformations for symmetry-nonequivalent chelate rings.[1] Unfortunately, such explanations are not easily extended to chelate ring carbon atoms where steric compression shifts are not expected, nor are they readily applied to complexes such as $[Co((\pm)\text{-bn})_3]^{3+}$ ("bn" = 2,3-butanediamine) whose diastereomers are easily distinguished by ^{13}C NMR even though the three chelate rings are expected to be rigid and to have very similar conformations.[1] Equally disconcerting is recent work showing exceptionally large chemical shift differences between diastereotopic carbon atoms in complexes of *cis*-1,2-cyclopentanediamine, a ligand expected to give rigid chelate rings with relatively fixed conformations.[6]

In order to determine what influence subtle electronic and steric effects might play in chemical shift differentiation of diastereotopic carbon atoms in complexes, we have separated the diastereomers of $[Rh((\pm)\text{-bn})_3]^{3+}$ and have determined their ^{13}C NMR spectra for comparison with (redetermined) spectra of $[Co((\pm)\text{-bn})_3]^{3+}$ isomers. A crystal structure of *lel,lel,lel*-$[Rh((\pm)\text{-bn})_3]Br_3$ has also been determined in order to compare the geometry of the cation with that found for $[Co((\pm)\text{-bn})_3]^{3+}$.[7]

Experimental Section

Synthesis. 2,3-Butanediamine was obtained commercially, and the meso and racemic isomers were separated as described elsewhere.[1] The racemic material as the dihydrochloride salt (9.66 g, 60 mmol) was dissolved in 50 mL of 80% aqueous methanol and was allowed to react with NaOH (4.8 g, 120 mmol) dissolved in a minimum of water. The NaCl precipitate was filtered off and the solution was added to aqueous $RhCl_3\cdot 3H_2O$ (2.63 g, 10 mmol). The mixture was heated on a steam bath and two more 60-mmol portions of (±)-2,3-butanediamine were added. After additional NaCl had precipitated, the solution was allowed to cool and isopropyl alcohol was added. The NaCl was removed by filtration, the solution was concentrated in vacuo with heating, and acetone was added to precipitate a mixture of $[Rh((\pm)\text{-bn})_3]Cl_3$ and excess ligand as the hydrochloride salt.

An aqueous solution of the precipitated mixture was chromatographed on SP Sephadex C-25 cation exchange resin on a 2.7 cm × 50 cm column using 0.5 M aqueous Na_2SO_4 eluent with a flow rate of 1 mL min^{-1}. Elution curves plotted from the spectral absorbances at 300 nm showed the presence of four chromatographic bands, which were identified as the *lel,lel,lel*, *lel,lel,ob*, *lel,ob,ob*, and *ob,ob,ob*

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