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Tetraacetanilidodichromium and -dimolybdenum: Another Supershort Chromium–Chromium Bond and an Unexpected Structural Difference

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The title compounds, $Cr_2[PhNC(O)CH_3]_4$, **1**, and $Mo_2[PhNC(O)CH_3]_4$, **2**, the first tetraamidodimetal compounds with quadruple M–M bonds, are described. They are prepared by reaction of the $M_2(O_2CCH_3)_4$ compounds with $Li[PhNC(O)CH_3]$. **1** was obtained as the unsolvated compound and the structure determined by X-ray crystallography. The crystals belong to space group $I\bar{4}$ with $a = 12.739$ (6) Å, $c = 9.251$ (3) Å, and $Z = 2$. Each molecule has $\bar{4}(S_4)$ crystallographic symmetry and the Cr–Cr distance is 1.873 (4) Å. The molybdenum compound, **2**, was also obtained in unsolvated form but crystals large enough for X-ray work could not be obtained. The bis(tetrahydrofuranate) $Mo_2[PhNC(O)CH_3]\cdot2THF$ did give suitable crystals, in space group $P2_1/c$ with $a = 9.849$ (2) Å, $b = 11.622$ (2) Å, $c = 17.957$ (2) Å, $\beta = 95.32$ (1)°, and $Z = 2$, in which each molecule resides on a crystallographic inversion center and has an Mo–Mo distance of 2.086 (2) Å. The ligand arrangement is different from that in **1**; the MoN_2O_2 groups have a cis configuration and the overall symmetry of the $Mo_2(NCO)_4$ grouping is C_{2h}. This is the first time homologous Cr_2^{4+} and Mo_2^{4+} complexes have been found to differ structurally in a qualitative way.

Introduction

In view of the extraordinary range of Cr–Cr distances so far observed in compounds containing the quadruply bonded Cr–Cr^{4+} unit, we have been extending our preparative endeavors to still further ligand types with the goal of elucidating the role played by the ligands in determining these distances. The problem we are addressing may be summarized as follows.

All tetracarboxylatodichromium(II) compounds[1] and related ones[2] whose structures have so far been determined have Cr–Cr distances in the range 2.29–2.53 Å.[3] The closely related $[Cr_2(CO_3)_4]^{4-}$ ion has a slightly shorter distance,[1c] 2.22 Å. These rather long distances have provoked controversy as to the Cr–Cr bond order.[4,5] On the other hand, there are a number of Cr_2 species in which the Cr–Cr distances are short enough that there has been no lack of agreement that they contain quadruple bonds. While two of these (with Cr–Cr distances in parentheses), namely, $[Cr_2(CH_3)_8]^{4-}$ (1.98 Å)[6] and $Cr_2(C_3H_5)_4$ (1.97 Å),[7] have been known for several years they are so different, at least superficially, from the $Cr_2(O_2CR)_4$ type that their general significance is (or was) ambiguous. A distinct dichotomy was created with the discovery[8] of a series of compounds, of which those in Table I are representative. These contain ligands that are sterically and electronically similar to the carboxylato group, and yet they have vastly shorter Cr–Cr bonds, i.e., in a range ≤1.90 Å, which we informally designate supershort.[9]

Our previous attempts to identify the ligand properties responsible for the occurrence of supershort Cr$\overset{4}{-}$Cr bonds have involved, inter alia, the following steps. (1) Compound **2** in Table I showed that the presence of Cr–C bonds is not critical, and compound **3** in Table I showed that Cr–O bonds are not in themselves essential. In short, no one type of ligand atom, C, N, or O, is critical. (2) Compound **4** in Table I showed that four noncarboxylato ligands are not necessary. (3) Compound **5** in Table I showed that it is not necessary for the Cr_2L_4 species to be a neutral molecule. (4) The one common feature of compounds 1–5 in Table I, namely, the incorporation of some ligand atoms in aromatic rings, was shown by compounds 6 and 7 in Table I not to be essential.

We report here a further crucial experimental step in achieving an understanding of what causes (or allows) the formation of supershort Cr$\overset{4}{-}$Cr bonds. We have prepared the first carboxamido-bridged dichromium compound, viz., $Cr_2[RNC(O)R']_4$ with $R = CH_3$ and $R' = C_6H_5$, and determined its structure X-ray crystallographically. We have also prepared the molybdenum analogue and determined its structure, with

Table I. Dichromium(II) Compounds Having Supershort Bonds and Their Cr–Cr Bond Lengths

no.	compd	bond length, Å	ref
1		1.85	8a
2		1.89	8b
3		1.87	8c
4		1.86	8d
5		1.83	8e
6		1.90	8f
7		1.86	8g

the surprising result that, for the first time, the two chemically homologous molecules are not structurally homologous.

Experimental Section

Preparation of $Cr_2[PhNC(O)CH_3]_4$, 1. Acetanilide (0.54 g, 4 mmol) was dissolved in 20 mL of tetrahydrofuran (THF) which had been dried over Na–K alloy, and 2.6 mL of a 1.6 M solution (4 mmol) of *n*-butyllithium in hexane was added, to give a solution containing the colorless anion $[C_6H_5NC(O)CH_3]^-$. Anhydrous $Cr_2(O_2CCH_3)_4$

Table II. Crystallographic Data

formula	$Cr_2(C_6H_5NC$-$(CH_3)O)_4$, 1	$Mo_2(C_6H_5NC$-$(CH_3)O)_4\cdot 2THF$, 2
space group	$I\bar{4}$	$P2_1/c$
a, Å	12.739 (6)	9.849 (2)
b, Å		11.622 (2)
c, Å	9.251 (3)	17.957 (2)
β, deg		95.32 (1)
V, Å³	1501 (1)	2047 (1)
d, g/cm³	1.42	1.41
Z	2	2
cryst size, mm	0.1 × 0.1 × 0.08	0.1 × 0.1 × 0.1
μ, cm⁻¹	8.02	6.53
range 2θ, deg	3 →45	3 →45
no. of unique data	509	1579
data with $F_o{}^2 >$ $3\sigma(F_o{}^2)$	446	1464
R_1 (anisotropic)^a	0.051	0.058
R_2 (anisotropic)^b	0.060	0.077
goodness of fit	1.09	1.55

^{a} $R_1 = (\Sigma ||F_o| - |F_c||)/\Sigma |F_o|$. ^{b} $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Figure 1. The $Cr_2[C_6H_5NC(O)CH_3]_4$ molecule. The atom numbering scheme is defined. The S_4 rotations generate suitably primed labels for all unlabeled atoms.

(0.34 g, 1 mmol) was added and the mixture was stirred overnight at room temperature. The amorphous precipitate of lithium acetate was removed by filtration and a layer of 10 mL of hexane was placed carefully over the orange THF solution. After 3 days of slow diffusion, yellow-orange crystals which had grown on the glass wall were collected for X-ray crystallography. Addition of a further 20 mL of hexane to the solution precipitated more of the compound to give a total yield of 70%. The dry product can be handled under atmospheric conditions for some hours. For $Cr_2[PhNC(O)CH_3]_4$, $C_{32}H_{32}N_4O_4Cr_2$, the calculated mass of the principal isotopic species is 640.123 360 and the mass spectrum gave an experimental value of 640.121 347.

Preparation of $Mo_2[PhNC(O)CH_3]_4$, 2. The procedure was essentially the same as that used for 1. However, the crystals obtained by slow diffusion of the hexane layer into the THF solution were too small for X-ray work. A THF solution was then evaporated in a continuous flow of argon to yield pale yellow crystals of sufficient size. These crystals were very air sensitive and proved to be the bis(tetrahydrofuranate), $Mo_2[PhNC(O)CH_3]_4\cdot 2THF$. The mass spectrum gave a peak at m/e 732.054 769 while the value calculated for the principal isotopic species of $C_{32}H_{32}N_4O_4Mo_2$ is 732.054 280.

X-ray Crystallography. Data Collection. A Syntex PĪ automated four-circle diffractometer using $Mo(\lambda\ 0.710\ 73\ Å)$ radiation with a graphite crystal monochromator in the incident beam was employed. Rotation photographs and ω scans of several strong reflections indicated in each case that the crystals were of satisfactory quality. The unit cell dimensions were obtained by a least-squares fitting of 15 strong reflections in the range $25° < 2\theta < 32°$. Data were collected at 22 ± 3 °C by using the θ–2θ scan technique with a variable scan rate from 4.0 to 24°/min. General procedures for data collection have been reported elsewhere.[10] Crystallographic data and other pertinent information are given in Table II. For each crystal, Lorentz and polarization corrections, but no absorption correction, were applied.

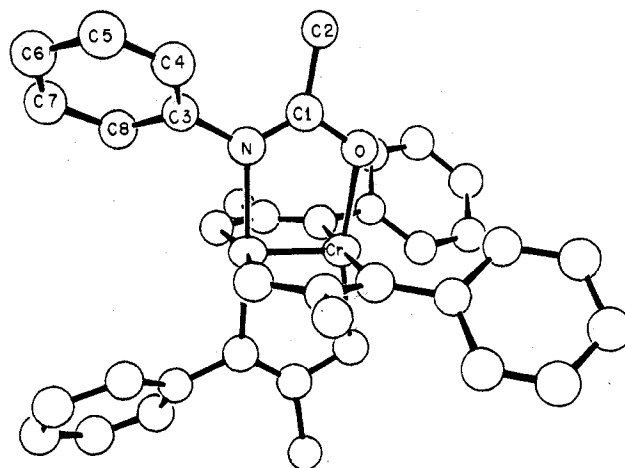**Solution and Refinement of the Structure.**[11] The heavy-atom positions were in each case obtained through a three-dimensional Patterson function. Structure 1 was refined in space group $I\bar{4}$ to convergence by using anisotropic thermal parameters for the chromium, oxygen, and nitrogen atoms and isotropic ones for all the carbon atoms. Hydrogen atoms were introduced at calculated positions and their contributions included in F_c values, but they were not refined. After refinement had converged for the (arbitrarily) chosen enantiomorph, the other one was refined and it was concluded that this was a better choice. The results presented here are for the second choice.

For the bis(tetrahydrofuranate) of 2 refinement proceeded smoothly to convergence in space group $P2_1/c$ by using anisotropic thermal vibration parameters for the molybdenum atom and the coordinated nitrogen and oxygen atoms and isotropic ones for the other atoms and omitting hydrogen atoms.

Final residuals are given in Table II, and tables of observed and calculated structure factors are available as supplementary material. In each case a final electron density difference map showed no significant peaks.

Results and Discussion

The atomic positional and thermal parameters are listed in Tables III and IV. The structures are shown and the atom numbering schemes defined in Figures 1 and 2. The important bond distances and angles are listed in Tables V and VI for the chromium and molybdenum compounds, respectively.

In compound 1 the $Cr_2[PhNC(O)CH_3]_4$ molecule resides upon a position of $\bar{4}(S_4)$ symmetry. Thus, as shown in Figure 1, the asymmetric unit consists of one chromium atom and one ligand, the rest of the molecule being generated from these by the improper rotation operations. The tilt of the phenyl ring plane abolishes the planes of symmetry inherent in the

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for 1

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	−0.5000 (0)	−0.5000 (0)	−0.6012 (2)	3.49 (8)	2.48 (7)	3.24 (7)	0.2 (1)	0	0
O	−0.4703 (5)	−0.6506 (5)	−0.3693 (6)	3.9 (3)	3.6 (3)	2.8 (3)	0.5 (2)	−0.5 (3)	0.4 (3)
N	−0.4621 (5)	−0.6572 (5)	−0.6108 (9)	3.1 (3)	2.2 (3)	4.2 (4)	0.4 (3)	−0.8 (4)	0.6 (4)

atom	x	y	z	B, Å²	atom	x	y	z	B, Å²
C(1)	−0.4549 (6)	−0.7043 (6)	−0.482 (1)	3.1 (2)	H(1)	−0.5708 (0)	−0.6410 (0)	−0.8422 (0)	5.0000 (0)
C(2)	−0.4361 (8)	−0.8218 (8)	−0.463 (1)	4.2 (2)	H(2)	−0.5381 (0)	−0.7056 (0)	−1.0724 (0)	5.0000 (0)
C(3)	−0.4418 (7)	−0.7033 (7)	−0.747 (1)	2.9 (2)	H(3)	−0.3838 (0)	−0.8006 (0)	−1.1178 (0)	5.0000 (0)
C(4)	−0.5096 (8)	−0.6820 (7)	−0.859 (1)	3.4 (2)	H(4)	−0.2703 (0)	−0.8398 (0)	−0.9297 (0)	5.0000 (0)
C(5)	−0.4898 (7)	−0.7191 (7)	−0.996 (2)	4.2 (2)	H(5)	−0.3013 (0)	−0.7754 (0)	−0.6982 (0)	5.0000 (0)
C(6)	−0.3990 (8)	−0.7766 (8)	−1.023 (1)	4.7 (2)	H(6)	−0.4337 (0)	−0.8381 (0)	−0.3626 (0)	5.0000 (0)
C(7)	−0.3311 (8)	−0.7986 (9)	−0.912 (1)	5.0 (2)	H(7)	−0.4916 (0)	−0.8599 (0)	−0.5071 (0)	5.0000 (0)
C(8)	−0.3498 (8)	−0.7617 (9)	−0.774 (1)	4.0 (2)	H(8)	−0.3712 (0)	−0.8406 (0)	−0.5066 (0)	5.0000 (0)

^{a} The form of the anisotropic thermal parameter is $\exp[-^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for 2

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0.0331 (1)	0.08076 (9)	0.01944 (5)	3.74 (4)	3.37 (4)	2.02 (3)	0.33 (6)	0.00 (3)	−0.20 (5)
O(1)	0.1506 (8)	0.1126 (6)	−0.0701 (4)	4.1 (4)	3.2 (4)	2.7 (3)	0.2 (3)	0.3 (3)	−0.4 (3)
O(2)	0.1336 (8)	−0.1681 (7)	0.0361 (4)	3.7 (4)	3.8 (4)	2.3 (3)	0.1 (4)	−0.2 (3)	−0.2 (3)
N(1)	0.0859 (9)	−0.0628 (8)	−0.1131 (5)	3.8 (4)	2.5 (4)	2.8 (4)	−0.1 (4)	0.3 (3)	−0.3 (3)
N(2)	0.2142 (10)	0.0015 (8)	0.0764 (5)	3.2 (5)	3.9 (5)	2.6 (4)	0.4 (4)	0.2 (3)	−0.2 (3)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O	0.141 (2)	0.320 (2)	0.0382 (9)	14.6 (5)	C(11)	0.319 (1)	0.073 (1)	0.1123 (6)	3.5 (2)
C(1)	0.159 (1)	0.030 (1)	−0.1191 (6)	3.5 (2)	C(12)	0.320 (2)	0.097 (1)	0.1889 (8)	5.9 (3)
C(2)	0.256 (1)	0.054 (1)	−0.1788 (7)	4.4 (3)	C(13)	0.426 (2)	0.168 (1)	0.2244 (9)	6.9 (4)
C(3)	0.090 (1)	−0.156 (1)	−0.1661 (6)	3.1 (2)	C(14)	0.523 (2)	0.213 (1)	0.1821 (8)	6.4 (4)
C(4)	0.127 (1)	−0.262 (1)	−0.1393 (6)	3.5 (2)	C(15)	0.521 (2)	0.189 (1)	0.1075 (8)	6.5 (4)
C(5)	0.134 (1)	−0.356 (1)	−0.1885 (7)	4.2 (3)	C(16)	0.419 (2)	0.116 (1)	0.0718 (8)	5.6 (3)
C(6)	0.092 (1)	−0.339 (1)	−0.2653 (7)	4.3 (3)	C(17)	0.190 (3)	0.386 (3)	−0.0283 (16)	14.9 (9)
C(7)	0.055 (1)	−0.232 (1)	−0.2918 (7)	4.6 (3)	C(18)	0.192 (3)	0.380 (3)	0.1114 (16)	15.8 (10)
C(8)	0.050 (1)	−0.140 (1)	−0.2424 (7)	4.4 (3)	C(19)	0.266 (3)	0.483 (3)	0.0830 (16)	15.4 (9)
C(9)	0.228 (1)	−0.110 (1)	0.0709 (6)	3.6 (3)	C(20)	0.278 (4)	0.482 (4)	0.0027 (22)	21.8 (15)
C(10)	0.352 (1)	−0.174 (1)	0.1047 (7)	4.2 (3)					

^{a} The form of the anisotropic thermal parameter is $\exp[-^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table V. Bond Distances and Bond Angles for
$Cr_2[C_6H_5NC(CH_3)O]_4$

Bond Distances, Å

Cr–Cr′	1.873 (4)	C(3)–N	1.41 (1)
O	1.972 (8)	C(4)	1.38 (1)
N	2.060 (9)	C(8)	1.41 (1)
C(1)–O	1.26 (1)	C(4)–C(5)	1.37 (2)
N	1.34 (1)	C(5)–C(6)	1.39 (1)
C(2)	1.52 (1)	C(6)–C(7)	1.37 (2)
		C(7)–C(8)	1.38 (1)

Bond Angles, Deg

Cr′–Cr–O	98.0 (2)	N–C(1)–C(2)	124 (1)
N	92.5 (3)	C(1)–N–C(3)	126.6 (9)
O–Cr–O′	164.1 (4)	Cr–N–C(3)	118.9 (7)
N	92.0 (4)	N–C(3)–C(4)	118.5 (9)
N′	87.3 (4)	C(8)	121.9 (9)
N–Cr–N′	175.1 (6)	C(4)–C(3)–C(8)	119 (1)
		C(3)–C(4)–C(5)	121 (1)
Cr–O–C(1)	116.2 (6)	C(4)–C(5)–C(6)	120 (1)
Cr–N–C(1)	114.4 (8)	C(5)–C(6)–C(7)	120 (1)
O–C(1)–N	118.9 (8)	C(6)–C(7)–C(8)	121 (1)
C(2)	117.0 (10)	C(7)–C(8)–C(3)	119.1 (9)

Table VI. Bond Distances and Bond Angles for
$Mo_2[C_6H_5NC(CH_3)O]_4\cdot2THF$

Bond Distances, Å

Mo′–Mo	2.086 (2)	Mo′–O(2)	2.10 (1)
O	2.990 (6)	N(1)	2.15 (2)
O(1)	2.10 (2)	N(2)	2.18 (1)
O(1)–C(1)	1.31 (2)	O(2)–C(9)	1.27 (1)
N(1)–C(1)	1.31 (1)	N(2)–C(9)	1.31 (1)
C(1)–C(2)	1.53 (1)	C(9)–C(10)	1.50 (1)
N(1)–C(3)	1.44 (2)	N(2)–C(11)	1.43 (2)
C(3)–C(4)	1.36 (1)	C(11)–C(12)	1.40 (2)
C(8)	1.40 (1)	C(16)	1.37 (2)
C(4)–C(5)	1.41 (1)	C(12)–C(13)	1.43 (2)
C(5)–C(6)	1.41 (1)	C(13)–C(14)	1.38 (2)
C(6)–C(7)	1.38 (2)	C(14)–C(15)	1.37 (2)
C(7)–C(8)	1.39 (1)	C(15)–C(16)	1.42 (2)
O–C(17)	1.53 (3)	C(20)–C(19)	1.46 (4)
C(18)	1.53 (3)	C(19)–C(18)	1.46 (4)
C(17)–C(20)	1.49 (4)		

Bond Angles, Deg

Mo′–Mo–O	166.6 (1)	O(1)–Mo–O(2)	90.7 (6)
O(1)	94.6 (2)	N(1)	175.3 (2)
O(2)	94.0 (2)	N(2)	87.0 (6)
N(1)	89.9 (2)	O(2)–Mo–N(1)	87.7 (6)
N(2)	89.6 (2)	N(2)	175.9 (2)
C(3)–C(8)–C(7)	119.8 (9)	N(1)–Mo–N(2)	94.2 (7)
Mo–O(1)–C(1)	117.3 (6)	Mo–O(2)–C(9)	118.8 (5)
Mo–N(1)–C(1)	119 (1)	Mo–N(2)–C(9)	118 (1)
O(1)–C(1)–N(1)	119 (1)	O(2)–C(9)–N(2)	119 (1)
C(2)	115 (1)	C(10)	118 (1)
N(1)–C(1)–C(2)	126 (1)	N(2)–C(9)–C(10)	123 (1)
Mo–N(1)–C(3)	119.6 (6)	Mo–N(2)–C(11)	119.4 (6)
C(1)–N(1)–C(3)	121 (2)	C(9)–N(2)–C(11)	122 (1)
N(1)–C(3)–C(4)	118 (1)	N(2)–C(11)–C(12)	120 (1)
C(8)	121 (1)	C(16)	120 (1)
C(3)–C(4)–C(5)	120.3 (8)	C(11)–C(12)–C(13)	119 (1)
C(4)–C(5)–C(6)	118.7 (9)	C(12)–C(13)–C(14)	119 (1)
C(5)–C(6)–C(7)	120.4 (9)	C(13)–C(14)–C(15)	120 (1)
C(6)–C(7)–C(8)	119.9 (9)	C(14)–C(15)–C(16)	121 (1)
		C(11)–C(16)–C(15)	119 (1)
		C(17)–O–C(18)	110 (1)
		O–C(18)–C(19)	101 (2)
		C(18)–C(19)–C(20)	115 (3)
		C(17)–C(20)–C(19)	106 (3)

Figure 2. The $Mo_2[C_6H_5NC(O)CH_3]_4$ molecule. The atom numbering scheme is shown.

five-membered Cr–Cr–N–C–O rings, but if this effect is neglected, it can be said that the essential core of the molecule, i.e., the $Cr_2[NC(O)C]_4$ unit, has virtual D_{2d} symmetry. The arrangement of ligating atoms about each metal atom is such

that N is trans to N and O is trans to O. However, the CrN_2O_2 set of atoms is distinctly nonplanar. The Cr′–Cr–N angles are 92.5 (3)° and the N–Cr–N′ chain (angle 175.1 (6)°) is nearly linear. The O–Cr–O′ chain, on the other hand, is distinctly bent, with an angle of 164.1 (4)°, and this is reflected in the Cr′–Cr–O angles of 98.0 (2)°. In effect, the

"bite" of the N–C–O group is larger than the Cr–Cr distance and the necessary increase in the Cr'–Cr–O and/or Cr'–Cr–N angles over 90° occurs mostly in the former.

The most important feature of this structure is the occurrence of another "supershort" Cr–Cr bond, 1.873 (4) Å. That this happens in a molecule with ligands so very similar to RCO_2^- is of great significance. The greatest difference between $CH_3C(O)NPh^-$ and $CH_3CO_2^-$ is the steric difference between PhN and O. The PhN groups make it impossible for the molecules to associate with each other through intermolecular O···Cr axial bonds, or to accommodate separate donor molecules as axial ligands, whereas *every* known tetracarboxylatodichromium molecule either is a disolvate with axial ligands, $Cr_2(O_2CR)_4L_2$, or has a structure in which the $Cr_2(O_2CR)_4$ molecules are arranged in infinite chains with intermolecular O···Cr axial distances of 2.22–2.44 Å. In nearly every other compound with a supershort Cr—⁴Cr bond the ligands prevent both axial coordination by separate donors and intermolecular association via axial bonds. For compound 4 in Table I it is likely that whether or not purely steric forces preclude axial coordination the high negative charge on the complex renders it unattractive to donor molecules. This may also be true of the $[Cr_2(CH_3)_8]^{4-}$ ion. In any case, it is a fact that there *are no axial bonds* in *any* of the compounds with Cr–Cr bonds and there *are axial* bonds in *every one* of the compounds with Cr–Cr bonds as long as or longer than 2.22 Å.

We must, therefore, consider very seriously the possibility that the dichotomy of supershort and long Cr—⁴Cr bonds is due solely to the absence or presence of axial ligands. For Mo—⁴Mo and Re—⁴Re bonds it is known[12] that axial coordination causes slight lengthening of the bonds; it is likely that Cr—⁴Cr bonds are far more sensitive in this respect.[1]

We feel that the electronic similarity of some ligands, especially $(PhN)OCCH_3^-$, to $O_2CCH_3^-$ is so great that the most crucial question about Cr_2^{4+} complexes is now set out in the starkest terms: Does the Cr–Cr quadruple bond length depend strongly only upon the presence or absence of axial ligands (which means that an isolated $Cr_2(O_2CR)_4$ molecule should have a Cr–Cr bond length ≤1.90 Å) or does a set of *four* O_2CR^- ligands have some special electronic property causing the Cr–Cr quadruple bond to be long and weak? For an answer to this question, the ultimate experimental step must be to observe a $Cr_2(O_2CR)_4$ molecule in the absence of any significant axial bonding. There would appear to be only two possible ways to do this. One is to devise some kind of R group capable of preventing axial coordination. The other is to conduct an electron diffraction measurement of the Cr–Cr bond length in the gas phase. Both of these approaches are being actively pursued.

Should it turn out that the Cr–Cr bonds in $Cr_2(O_2CR)_4$ molecules free of axial bonds are supershort, the ab initio theoretical treatment of these substances will once again be in profound difficulties. Even though the absurd notion that no Cr–Cr bond exists[4a] has been abandoned, it is currently asserted that such a bond has its maximum strength at a distance of ca. 2.40 Å.[4b]

In compound **2** the $Mo_2[PhNC(O)CH_3]_4$ molecule resides on a center of inversion. Hence, the asymmetric unit here consists of one metal atom and two ligands, as shown in Figure 2. The THF molecules are not coordinated to the molybdenum atoms. The closest contact is between Mo and the O atom of THF at a distance of 2.990 (6) Å, with an Mo'–Mo–O angle of 166.6 (1)°. The structural details within each Mo–Mo–N–C–O ring are quite similar to those for the rings in the chromium compound. Each such ring is essentially planar and

again the phenyl ring plane is tilted with respect to it. The bonds about each carboxyl carbon atom and each amido nitrogen atom are again coplanar within experimental error. The Mo'–Mo–N angles are much closer to 90° than are the Mo'–Mo–O angles, which is qualitatively analogous to the situation in the chromium compound but quantitatively not so extreme because the longer Mo–Mo distance is closer to the "bite" of the ligand. Thus, the Mo'–Mo–O angles are only 94.3 (2)°.

The striking difference between the structures of **1** and **2** is in the overall symmetry of the arrangement of the ligands about the dimetal unit. In **2**, the MoN_2O_2 sets have the cis configuration, and the virtual symmetry of the $Mo_2(NCO)_4$ unit is C_{2h}. In earlier studies[13] where the ligands have two different donor atoms, the D_{2d} arrangement has been observed in all cases where the ligating atoms were N and O, N and N' (but not equivalent), or N and S. Only for the cases where the ligating atoms were C and O has the cis (C_{2h}) configuration been found. In every case where the structures of the chromium and molybdenum compounds have both been determined, they have had the same configuration. Qualitative arguments based on inspection and measurement of scale models do not indicate any marked preference based on steric considerations for either the D_{2d} or the C_{2h} arrangement. From that point of view the occurrence of the former in **1** and the latter in **2** is not surprising. However, there might also be electronic factors favoring one or the other and the results we have obtained suggest that these are either (1) always small or (2) variable depending on whether the metal atoms come from the first or second transition series. Further discussion of this matter seems to be unwarranted at present.

Supplementary Material Available: Tables of observed and calculated structure factors for both structures (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Cotton, F. A.; Extine, M. W.; Rice, G. W. *Inorg. Chem.* 1978, *17*, 176. (b) Cotton, F. A.; Rice, G. W. *Ibid.* 1978, *17*, 688. (c) Cotton, F. A.; Rice, G. W. *Ibid.* 1978, *17*, 2004.
(2) The carbamato complex $Cr_2(O_2CNEt_2)_4$ is also in this category [Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Rideout, D. C. *Inorg. Chem.* 1978, *17*, 3536] and ref 1c includes the carbonato compound.
(3) Esd's on all Cr–Cr distances are in the third decimal place; we shall state them here to the nearest 0.01 Å, a figure which is, therefore always reliable, even, in most cases, to within the 3σ criterion.
(4) (a) Garner, C. D.; Hillier, I. H.; Guest, M. F.; Green, J. C.; Coleman, A. W. *Chem. Phys. Lett.* 1976, *41* 91. (b) Benard, M.; Viellard, A. *Nouv. J. Chim.* 1977, *1*, 97. (c) Guest, M. F.; Hillier, I. H.; Garner, C. D. *Chem. Phys. Lett.* 1977, *48*, 587.
(5) Cotton, F. A.; Stanley, G. G. *Inorg. Chem.* 1977, *16*, 2668.
(6) Krausse, J.; Marx, G.; Schödl, G. *J. Organomet. Chem.* 1970, *21*, 159. The closely similar $[Cr_2(CH_2CH_2CH_2CH_2)_4]^{4-}$ ion with essentially the same Cr–Cr distance has also been described: Krausse, J.; Schödl, G. *J. Organomet. Chem.* 1971, *27*, 59.
(7) Albrecht, G. A.; Stock, D. *Z. Chem.* 1967, *7*, 231. Aoki, T.; Furusaki, A.; Tomiie, Y.; Ono, K.; Tanaka, K. *Bull. Chem. Soc. Jpn.* 1969, *42*, 545.
(8) (a) Cotton, F. A.; Koch, S.; Millar, M. *J. Am. Chem. Soc.* 1977, *99*, 7372; *Inorg. Chem.* 1978, *17*, 2087. (b) Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* 1978, *100*, 4725. (c) Cotton, F. A.; Niswander, R. H.; Sekutowski, J. C. *Inorg. Chem.* 1978, *17*, 3541. (d) Cotton, F. A.; Millar, M. *Ibid.* 1978, *17*, 2014. (e) Cotton, F. A.; Koch, S. *Ibid.* 1978, *17*, 2021. (f) Cotton, F. A.; Hanson, B. E.; Rice, G. W. *Angew. Chem.* 1978, *90*, 1015. *Angew. Chem., Int. Ed. Engl.* 1978, *17*, 953. (g) Cotton, F. A.; Rice, G. W.; Sekutowski, J. C. *Inorg. Chem.* 1979, *18*, 1143.
(9) The choice of 1.90 Å as a line of demarcation, though somewhat arbitrary, is not entirely so. For one thing, it does in fact constitute the approximate upper limit of bond lengths in all the compounds we wish to deal with. For another, a distance of ca. 1.90 Å (actually 1.89 Å to be exact) corresponds to the formal shortness ratio[8a] of 0.80 below which no metal–metal bonds (or *any others* save N≡N and C≡C) except

these particular $Cr\overset{4}{-}Cr$ bonds have ever been observed.

(10) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227. Adams, R. D.; Collins, D. M.; Cotton, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 749.

(11) All crystallographic computing was done on a PDP 11/45 computer at the Molecular Structure Corp., College Station, Texas, using the Enraf-Nonius structure determination package.

(12) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1977**, *16*, 1867.

(13) See for full references: Cotton, F. A.; Niswander, R. H.; Sekutowski, J. C. *Inorg. Chem.* **1979**, *18*, 1152.

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Crystal Structure of ((S)-Malato)tetraaquamagnesium(II) Hydrate. Versatility of (S)-Malate–Metal Ion Binding

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The crystal structure of ((S)-malato)tetraaquamagnesium(II) hydrate, [Mg(S-C$_4$H$_4$O$_5$)(H$_2$O)$_4$]·H$_2$O, has been determined from three-dimensional single-crystal X-ray diffraction data collected by counter methods on a computer-automated diffractometer. The compound crystallizes in the orthorhombic space group D_2^4-P2$_1$2$_1$2$_1$ with unit cell dimensions a = 11.403 (9) Å, b = 15.486 (10) Å, c = 5.954 (4) Å, and Z = 4. The structure was solved by direct methods and refined by a full-matrix least-squares procedure to a conventional R index of 0.081 for 1248 reflections. The bidentate (S)-malate ligand chelates the magnesium(II) ion with an α-carboxylate oxygen atom and the hydroxyl oxygen forming a planar five-membered chelate ring. The irregular octahedral coordination polyhedron around the metal ion is completed by four water molecules. The β-carboxylate group is not bound directly to Mg(II) which differs from (S)-malate binding observed in all other 1:1 metal (S)-malate compounds. However, the β-carboxylate group is indirectly attached to the Mg(II) in an outer-sphere fashion through an intramolecular hydrogen bond from a coordinated water molecule. The conformation of the (S)-malate ligand is synclinal, and the range in Mg–O bond lengths is 2.045 (5)–2.125 (5) Å.

Introduction

As part of a continuing study of the structural characteristics of carboxylate–metal ion binding, we have been interested in the coordination chemistry of naturally occurring hydroxy acids such as (S)-malic acid, HOOCCHOHCH$_2$COOH. The flexibility of (S)-malate binding to metal ions has been demonstrated from the crystal structural investigations of the 1:1 complexes of manganese(II),[1] zinc(II),[2] cobalt(II),[3] and calcium(II).[4] There has also been a report on the structure of a 2:1 oxomolybdenum(VI) complex.[5] In these instances the (S)-malate ligand is found to adopt different conformations as well as different modes of metal ion binding. Four-, five-, and six-membered chelate rings have all been observed. The carboxylate interactions encountered in such structures contribute to the understanding of the coordination chemistry of metal ions in biological systems. In particular, magnesium(II) ion is known to be required in many enzyme-catalyzed reactions, but accurate structural details of magnesium(II) complexes with simple biological metabolites are lacking. It is anticipated that oxygen atoms and carboxylate groups would be strongly implicated in the binding of such "hard" cations.[6] We report here the crystal structure of ((S)-malato)tetraaquamagnesium(II) hydrate which reveals a unique mode of (S)-malate binding and further establishes the versatility of (S)-malate–metal ion coordination.

Experimental Section

Well-formed colorless single crystals of the title compound were grown by evaporation of a solution prepared by dissolving magnesium carbonate in an aqueous solution of (−)-malic acid (Eastman). A crystal with approximate dimensions 0.22 × 0.34 × 0.40 mm, which gave sharp optical extinction under crossed polarizers, was mounted along the longest crystal dimension. Examination of indexed Weissenberg photographs revealed orthorhombic symmetry, and the observed pattern of systematically absent reflections, h odd for $h00$, k odd for $0k0$, and l odd for $00l$, uniquely indicated the space group to be P2$_1$2$_1$2$_1$. The unit cell dimensions were determined at 23 ± 2 °C from a least-squares refinement of the angular settings of 12 carefully centered reflections measured with a Picker FACS-I

computer (PDP-8/L) automated diffractometer using Mo Kα radiation (λ 0.710 69 Å).

Crystal data for [MgC$_4$H$_4$O$_5$(H$_2$O)$_4$]·H$_2$O: orthorhombic; space group P2$_1$2$_1$2$_1$; a = 11.403 (9), b = 15.486 (10), c = 5.954 (4) Å; V = 1051.4 Å^3; Z = 4; d_m = 1.54 (1) (by flotation), d_c = 1.557 g/mL; $F(000)$ = 520; μ(Mo Kα) = 2.2 cm^{-1}.

Data Collection. Three-dimensional intensity data were collected out to 55° in 2θ by using zirconium-filtered Mo Kα radiation. The $\theta/2\theta$ scan mode with a fixed rate of 1°/min and a scan range of 2θ(Mo Kα$_1$) − 1.0° to 2θ(Mo Kα$_2$) + 1.0° were used. The background counting time was 40 s at the start and end of each scan. The intensities of two standard reflections were monitored after each 100 reflections to check on crystal and electronic instability. A uniform increase in intensity of 13% was observed during the time that approximately half of the reflections were collected, but no variation occurred in the intensities of the standards for the remainder of the data set. A suitable correction was applied to the affected part of the data. Absorption corrections were judged to be negligible in view of the small absorption coefficient and dimensions of the crystal. The raw intensity data were assigned standard deviations and reduced to values of F_o and $\sigma(F_o)$ by using $I = C - (t_c/2t_b)(B_1 + B_2)$, $F_o = (I/Lp)^{1/2}$, $\sigma(I) = [C + (t_c/2t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$, and $\sigma(F_o) = (2F_o)^{-1}(Lp)^{-1}\sigma(I)$. In these expressions C is the total count accumulated during the scan in time t_c, B_1 and B_2 are the background counts at each end of the scan each in a time t_b, and p is taken to be 0.04. A total of 1248 reflections had $I > \sigma(I)$, and these were used in subsequent calculations.

Solution and Refinement of the Structure[7]

The structure was solved by direct methods using MULTAN. The positions of all the nonhydrogen atoms were readily evident from an E map generated from the solution of the highest figure of merit and lowest residual. The absolute configuration of the (−)-malate ligand was fixed to be S.[3] After initial isotropic and then anisotropic refinement of the nonhydrogen atoms by a full-matrix procedure, a difference Fourier synthesis revealed the positions of all the hydrogen atoms. Each hydrogen atom was assigned an isotropic thermal parameter 1.0 Å^2 greater than the isotropic thermal parameter of the atom to which the hydrogen is attached. The entire structure was further refined by full-matrix least squares although the hydrogen atom parameters were not varied. A total of 136 parameters including one scale factor were refined yielding a data:parameter ratio of 9.2:1.