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Two Quadruply Bonded Amino Acid Complexes of Dichromium(II): Structures of Tetrakis(glycine)tetrabromodichromium(II) Tetrahydrate and Tetrakis(glycine)tetrachlorodichromium(II) Trihydrate

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Glycine in oxygen-free aqueous acid solutions of chromous halides coordinates in its zwitterionic form, $^{-}O_2CCH_2NH_3^{+}$, to give carboxylate-bridged Cr_2^{4+} complexes. These complexes precipitate from concentrated solutions as air-stable hydrated purple crystalline salts of the general formula $Cr_2(O_2CCH_2NH_3)_4X_4 \cdot nH_2O$, and the structures of two of these compounds (**1**, X = Br, $n = 4$; **2**, X = Cl, $n = 3$) were investigated by single-crystal X-ray diffraction techniques. Crystals of **1** belong to the triclinic space group $P\bar{1}$ with 1 formula weight in a cell of dimensions $a = 8.455$ (1) Å, $b = 11.340$ (2) Å, $c = 6.799$ (1) Å, $\alpha = 98.74$ (3)°, $\beta = 104.38$ (2)°, $\gamma = 77.68$ (3)°, and $V = 613$ (1) Å^3. Least-squares refinement of 1751 reflections with $I > 3\sigma(I)$ produced final discrepancy factors of $R_1 = 0.036$ and $R_2 = 0.042$. The structure consists of centrosymmetric $[Cr_2(O_2CCH_2NH_3)_4]^{4+}$ cations approximating D_{4h} symmetry and containing a Cr–Cr bond of 2.513 (1) Å in length, axial Br^- ions at 2.736 (1) Å from the Cr atoms and nearly collinear to the Cr–Cr bond, and another unique Br^- ion and two unique water molecules that reside on general positions in the unit cell. The zwitterionic glycine molecules form intramolecular hydrogen bonds averaging 2.69 Å in length between the terminal nitrogen atom of the NH_3^+ group and one of the bridging carboxylate oxygen atoms. Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with 2 formula units in a cell with dimensions $a = 8.325$ (1) Å, $b = 9.307$ (1) Å, $c = 14.675$ (2) Å, $\beta = 103.27$ (3)°, and $V = 1107$ (1) Å^3. This compound is isomorphous to the corresponding molybdenum complex. Refinement of the structure by least-squares methods using 1187 reflections with $I > 3\sigma(I)$ gave final discrepancy indices of $R_1 = 0.062$ and $R_2 = 0.072$. The $[Cr_2(O_2CCH_2NH_3)_4]^{4+}$ cations reside on crystallographic centers of inversion with a slightly longer Cr–Cr bond length than in **1** with a value of 2.524 (1) Å. One of the two Cl^- ions in the asymmetric unit occupies the axial position of the centrosymmetric dichromium cation with a Cr–Cl bond distance of 2.581 (1) Å. The other Cl^- ion resides on a general position in the unit cell with hydrogen-bonding interactions between the NH_3^+ groups of the glycine ligands and the water molecules that also are found in general positions in the unit cell. As was seen in **1** intramolecular hydrogen bonding occurs within the glycine ligands in **2** with an average N···O distance of 2.70 Å.

Introduction

Over the past few years, an extensive aqueous chemistry of molybdenum has developed[3] consisting of di- and trinuclear species of which the corresponding chromium complexes are unknown. X-ray crystallography has elucidated the structures of many of these new molybdenum species including cationic triangular clusters of the general formula $[Mo_3(\mu_3\text{-}X)(\mu_3\text{-}Y)(O_2CR)_6(H_2O)_3]^{n+}$, with R = CH_3 and X = Y = O,[4,5] X = O and Y = CCH_3,[4,6] or X = Y = CCH_3,[4,7] and anionic hydrido-bridged $[Mo_2Cl_8H]^{3-}$ species.[8,9] For chromium, trinuclear complexes involving oxidation states higher than +2 have been found, but these are limited to the μ_3-O centered triangular arrays[10,11] in which no metal to metal bonding occurs between Cr atoms. In 1976 it was discovered that aqueous acid solutions of Mo_2^{4+} have a strong affinity to form carboxylate-bridged complexes as shown in the structure of $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2 \cdot 4H_2O$.[12] Subsequent work established that other amino acids also form carboxylate-bridged dinuclear complexes of Mo_2^{4+} including L-isoleucine,[13] glycylglycine,[14] and L-leucine.[15] In each structure the amino acid is found in its zwitterionic form with only the carboxylate group coordinated to the dinuclear metal atoms while the remainder of the amino acid adopts its conformationally free configuration.

In light of the above examples in which several amino acids form crystalline complexes with Mo_2^{4+}, the possibility that analogous complexes would form with other dinuclear metal atoms was deemed high. Indeed, a recent report described the synthesis and molecular structure of a β-alanine complex with Rh_2^{4+} to give cations of $[Rh_2(O_2CCH_2CH_2NH_3)_4(H_2O)_2]^{4+}$.[16] Within the group 6 triad, Cr(II) readily complexes with carboxylic acids to give $Cr_2(O_2CR)_4L_2$ compounds.[3] Several years ago glycine was reported[17,18] to form two types of compounds with Cr(II), but detailed structural data are lacking. In the first of these compounds prepared by Herzog and Kalies,[18] addition of a deoxygenated $CrBr_2$ solution to sodium glycinate precipitates a light blue crystalline compound that analyzes as $Cr(O_2CCH_2NH_2)_2 \cdot H_2O$. Magnetic susceptibility data on this solid give a magnetic moment of 4.58 μ_B consistent with the presence of *mononuclear* high-spin Cr^{2+} with four unpaired electrons. Recent thermodynamic data[19] on complex formation between Cr^{2+} and glycine in solutions with a pH of from 4 to 8 reveal that an O,N-bonded chelate of glycine forms in this pH range in accord with analytical and magnetic data. However, another compound was reported by Herzog and Kalies[18] that is derived from the addition of free glycine to an aqueous acid solution of $CrBr_2$. The purple crystalline compound was formulated on the basis of its analysis as "$Cr(O_2CCH_2NH_2)_2 \cdot 2HBr \cdot 2H_2O$". Magnetic data show a depressed magnetic moment at 293 K of 0.79 μ_B suggestive of a strong magnetic exchange interaction between Cr^{2+} ions. In aqueous solution the purple solid dissolves to give a blue solution with a μ_{eff} value of 4.83 μ_B.

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In this paper we reinvestigated the product formed upon addition of glycine to aqueous acid solutions of chromous halides. The results described herein are consistent with the observations of Herzog and Kalies.[18] Crystalline products were obtained from the reaction mixtures for both $CrBr_2$ and $CrCl_2$ solutions. The structures as determined by X-ray crystallography provide the first unequivocal examples of amino acid complexes with Cr_2^{4+} and are reported in detail here.

Experimental Section

Compound Preparation. All manipulations involving chromous halide solutions were conducted under an atmosphere of argon or nitrogen. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

$Cr_2(O_2CCH_2NH_3)_4Br_4\cdot 4H_2O$ (1). To a 250-mL three-necked flask fitted with a stopcock, septum, and filter tube with adapter and collection flask was added a stir bar, 3.5 mL of water, and 9.6 mL of 48% HBr (5.69×10^{-2} mol, Mallinckrodt). After deoxygenation, 2.02 g of Cr metal (3.88×10^{-2} mol, Fisher, below 100 mesh) was added and the mixture stirred for ~3 h to give a blue solution of $CrBr_2$. In a separate 250-mL flask fitted with a stopcock and septum, 8.03 g of glycine (1.07×10^{-1} mol, Fisher) was dissolved in ~30 mL of water that was deoxygenated and then heated near the boiling point. The hot glycine solution was transferred with the use of a cannula into the $CrBr_2$ solution, producing a purple solution that soon deposited a fine violet precipitate. The solid was then warmed to 70 °C to dissolved it and then rapidly filtered through a 30-mL fritted medium-porosity filter into a 500-mL flask with stopcock. The hot solution was allowed to cool slowly overnight. During this time a mass of dichroic red–purple crystals deposited, which were for the most part badly twinned. However, a few irregular prisms were isolated that were suitable for X-ray crystallographic work (vide infra). Once the solid formed, the mixture was filtered in air and washed with ethanol; yield 4.11 g (26.8%). A second drop of purple material precipitated from the filtrate (10.30 g (66.7%)) to give a total yield of 15.44 g (93.5%). Analysis of the red-purple crystals was in agreement with the formula of **1**. Anal. Calcd for $Br_4Cr_2O_{12}N_4C_8H_{28}$: Br, 40.16; Cr, 13.07; N, 7.04; C, 12.07; H, 3.55. Found: Br, 40.38; Cr, 13.29; N, 6.95; C, 12.04; H, 3.29.

$Cr_2(O_2CCH_2NH_3)_4Cl_4\cdot 3H_2O$ (2). This compound is reported here for the first time and was prepared from a procedure analogous to that of the bromide complex **1**. The compound is more soluble in water than **1** and as such was prepared in smaller quantities. Deep purple faceted crystals were obtained after mixing the $CrCl_2$ and glycine solutions with a cubelike morphology but almost always twinned. The formula stated above was derived by structure solution of the X-ray diffraction data.

X-ray Crystallography. Data Collection, Structure Solution, and Refinement. Crystals of **1** and **2** were attached to glass fibers, coated with epoxy cement, and mounted on a Philips PW 1100 four-circle computer-controlled diffractometer for examination. X-ray data were collected on suitable crystals, and the crystallographic paramters and data collection procedures are summarized in Table I. Details of the data collection and reduction techniques have appeared before.[20] For **1** an absorption coefficient of 72.80 cm^{-1} suggested the possibility of a need for an absorption correction. However, a ψ scan about the 0.15-mm dimension of the prismatic crystal showed variations of only about ±10% in the diffracted intensity, and as such no absorption correction was applied. For crystal **2**, the low absorption coefficient and the nearly equidimensional size of the crystal obviated the need for an absorption correction.

Table I. Crystallographic Data and Data Collection Procedures

parameter	1	2
formula	$Br_4Cr_2O_{12}N_4C_8H_{28}$	$Cr_2Cl_4O_{11}N_4C_8H_{26}$
space group	$P1$	$P2_1/c$
a, Å	8.455 (1)	8.325 (1)
b, Å	11.340 (2)	9.307 (1)
c, Å	6.799 (1)	14.675 (2)
α, deg	98.74 (3)	90.
β, deg	104.38 (2)	103.27 (3)
γ, deg	77.68 (3)	90.
V, Å^3	613 (1)	1107 (1)
d_{calcd}, g/cm^3	2.16	1.80
Z	1	2
fw	795.936	600.117
cryst size, mm	$0.15 \times 0.10 \times 0.10$	$0.10 \times 0.10 \times 0.15$
μ(Mo Kα), cm^{-1}	72.80	14.28
radiation (λ, Å)	graphite-monochromated Mo Kα (0.71069)	
scan type	$\omega-2\theta$	$\omega-2\theta$
data collcn range	$\pm h,\pm k,+l$ ($3° \leq 2\theta \leq 50°$)	$\pm h,+k,+l$ ($3° \leq 2\theta \leq 45°$)
no. of unique data	2128	1425
no. of data, $F_o^2 > 3\sigma(F_o^2)$	1751	1187
no. of variables	136	131
R_1	0.036	0.062
R_2	0.042	0.072

The structures of both **1** and **2** were solved by heavy-atom techniques from three-dimensional Patterson maps.[21] Subsequent least-squares refinement followed by difference Fourier maps led to the location of all non-hydrogen atoms in each structure. In **1** all 15 non-hydrogen atoms were assigned anisotropic thermal parameters and all parameters were refined until $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ had the values shown in Table I. For structure **2** 14 of the 15 non-hydrogen atoms were assigned anisotropic thermal parameters. The remaining atom, OW(2), was assigned an occupancy factor of 0.5 and refined with an isotropic thermal parameter. The refinement converged at the discrepancy factors shown in Table I. No attempt was made to locate the hydrogen atoms in either structure, and the final difference Fourier maps contained no peaks of chemical significance. Tables of observed and calculated structure factor amplitudes for those reflections with $I > 3\sigma(I)$ are available.[22]

Results

The final positional parameters for **1** and **2** appear in Tables II and III, respectively. Anisotropic thermal parameters are listed in Tables IIA and IIIA.[22] Bond distances and angles for **1** and **2** are given in Tables IV and V, respectively, and these include some important intramolecular hydrogen-bonded contacts as well. Additional hydrogen-bonded contacts are tabulated in Tables IVA and VA.[22] Both structures **1** and **2** consist of a central $Cr_2(O_2CC)_4$ core that displays essentially D_{4h} symmetry. Halide ions appear nearly collinear with and at each end of the Cr–Cr bonds, with long Cr–X distances indicative of very weak bonding. Another halide ion resides in a general position in the crystal lattices along with two independent water molecules. These water molecules in conjunction with the terminal NH_3^+ groups on each glycine molecule form a tight hydrogen-bonding network throughout the crystal lattices in **1** and **2**. A detailed description of each structure will now be presented.

$Cr_2(O_2CCH_2NH_3)_4Br_4\cdot 4H_2O$ (1). One formula unit comprises the unit cell contents, with the entire molecule residing on a crystallographic center of inversion with the inversion center located at the midpoint of the Cr–Cr bond. Figure 1 depicts the structure of the $[Cr_2(O_2CCH_2NH_3)_4Br_2]^{2+}$ cations. These cations consist of a central Cr_2^{4+} dimetal unit having a Cr–Cr bond of 2.513 (1) Å in length. The Br^- ions occupy axial positions about each Cr atom at 2.736 (1) Å from the Cr centers and almost collinear to the Cr–Cr bond bond with a Cr′–Cr–Br(1) angle of 179.14 (5)°. Four glycine carboxyl groups bridge the dichromium(II) unit in the typical geometry[3] observed for $Cr_2(O_2CR)_4$ structures. The four Cr–O bonds that form square planes about the Cr atoms average 2.023 (5) Å in length, show little variation, and are in accord with values seen in other $Cr_2(O_2CR)_4L_2$ structures.

Closely similar dimensions are seen within the two glycyl residues in **1**. The bond lengths between non-hydrogen atoms appear normal. All of the non-hydrogen atoms assume an

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[21] All structure solution and refinement calculations were performed on a CYBER 74 computer at The Hebrew University of Jerusalem with the use of the SHELX 77 structure determination package.

[22] Supplementary material.

Table II. Atomic Positional Parameters for $Cr_2(O_2CCH_2NH_3)_4Br_4 \cdot 4H_2O$ (1)[a]

atom	x	y	z	atom	x	y	z
Cr	0.3912 (1)	0.04168 (9)	0.3520 (1)	N(2)	0.1984 (7)	0.3717 (5)	0.7955 (9)
Br(1)	0.15789 (8)	0.13233 (6)	0.0268 (1)	OL(1)	0.0736 (7)	0.3865 (7)	0.3661 (8)
Br(2)	0.2295 (1)	0.59071 (7)	0.1969 (1)	OL(2)	0.6273 (7)	0.4307 (5)	0.3065 (8)
O(1)	0.5748 (5)	0.1142 (4)	0.2985 (7)	C(1)	0.7196 (7)	0.0939 (6)	0.4038 (9)
O(2)	0.3352 (6)	0.1875 (4)	0.5518 (7)	C(2)	0.8558 (8)	0.1406 (6)	0.344 (1)
O(3)	0.2316 (5)	−0.0370 (4)	0.4398 (7)	C(3)	0.4162 (8)	0.1969 (6)	0.733 (1)
O(4)	0.4627 (5)	−0.1175 (4)	0.1894 (7)	C(4)	0.3751 (8)	0.3105 (6)	0.870 (1)
N(1)	0.7884 (7)	0.1992 (5)	0.1495 (8)				

[a] Estimated standard deviations for the least significant figures are given in parentheses and appear in this fashion in succeeding tables.

Table III. Atomic Positional Parameters for $Cr_2(O_2CCH_2NH_3)_4Cl_4 \cdot 3H_2O$ (2)

atom	x	y	z	atom	x	y	z
Cr	0.5655 (1)	0.6213 (1)	0.49517 (7)	N(2)	0.4545 (7)	0.4581 (6)	0.8263 (4)
Cl(1)	0.7018 (2)	0.8709 (2)	0.4992 (1)	C(1)	0.7880 (8)	0.3801 (6)	0.5484 (4)
Cl(2)	0.8247 (3)	0.1458 (3)	0.3316 (2)	C(2)	0.9585 (8)	0.3163 (8)	0.5635 (5)
O(1)	0.5655 (5)	0.5719 (5)	0.3597 (3)	C(3)	0.4919 (8)	0.5474 (7)	0.6739 (4)
O(2)	0.5502 (6)	0.6437 (5)	0.6300 (3)	C(4)	0.490 (1)	0.5855 (7)	0.7730 (5)
O(3)	0.7812 (5)	0.5141 (5)	0.5374 (3)	OW(1)	0.100 (1)	0.541 (2)	0.7626 (8)
O(4)	0.3335 (5)	0.7012 (5)	0.4550 (3)	OW(2)	0.850 (2)	0.753 (2)	0.732 (1)
N(1)	0.9524 (7)	0.1551 (7)	0.5614 (5)				

Table IV. Selected Bond Distances (Å) and Angles (deg) for $Cr_2(O_2CCH_2NH_3)_4Br_4 \cdot 4H_2O$ (1)[a]

	Distances		
Cr–Cr′	2.513 (1)	O(2)–C(3)	1.251 (7)
–Br(1)	2.736 (1)	O(3)′–C(1)	1.261 (8)
–O(1)	2.032 (5)	O(4)′–C(3)	1.273 (7)
–O(2)	2.024 (4)	OL(1)···N(2)	2.860 (7)
–O(3)	2.011 (5)	OL(2)···N(1)	2.868 (7)
–O(4)	2.024 (4)	N(1)–C(2)	1.495 (8)
O(1)···N(1)	2.674 (8)	N(2)–C(4)	1.502 (7)
O(1)–C(1)	1.248 (6)	C(1)–C(2)	1.53 (1)
O(2)···N(2)	2.701 (7)	C(3)–C(4)	1.499 (8)
	Angles		
Cr′–Cr–Br(1)	179.14 (5)	Cr–O(3)–C(1)′	119.6 (4)
–O(1)	84.9 (2)	Cr–O(4)–C(3)′	121.5 (5)
–O(2)	86.2 (2)	C(2)–N(1)···O(1)	62.8 (6)
–O(3)	87.3 (2)	···OL(2)	99.6 (6)
–O(4)	85.9 (2)	O(1)···N(1)···OL(2)	83.6 (5)
Br(1)–Cr–O(1)	94.3 (1)	C(4)–N(2)···O(2)	61.2 (6)
–O(2)	94.3 (2)	···OL(1)	118.7 (6)
–O(3)	93.4 (2)	O(2)···N(2)···OL(1)	64.8 (5)
–O(4)	93.7 (2)	O(1)–C(1)–O(3)′	126.5 (5)
O(1)–Cr–O(2)	90.6 (2)	–C(2)	119.1 (6)
–O(3)	172.2 (2)	O(3)′–C(1)–C(2)	114.4 (6)
–O(4)	91.7 (2)	N(1)–C(2)–C(1)	110.4 (6)
O(2)–Cr–O(3)	88.0 (2)	O(2)–C(3)–O(4)′	124.6 (7)
–O(4)	171.5 (2)	–C(4)	119.1 (7)
O(3)–Cr–O(4)	88.6 (2)	O(4)′–C(3)–C(4)	116.3 (7)
Cr–O(1)–C(1)	121.5 (4)	N(2)–C(4)–C(3)	110.4 (6)
Cr–O(2)–C(3)	121.7 (4)		

[a] Hydrogen-bonded contacts are given by dotted lines (···) between atoms in this and the following table.

Table V. Selected Bond Distances (Å) and Angles (deg) for $Cr_2(O_2CCH_2NH_3)_4Cl_4 \cdot 3H_2O$ (2)

	Distances		
Cr–Cr′	2.524 (1)	O(2)–C(3)	1.264 (8)
–Cl(1)	2.581 (1)	O(3)–C(1)	1.257 (7)
–O(1)	2.041 (4)	O(4)′···N(1)	2.692 (7)
–O(2)	2.022 (4)	O(4)′–C(1)	1.255 (8)
–O(3)	2.023 (4)	N(1)–C(2)	1.501 (9)
–O(4)	2.027 (4)	N(2)–C(4)	1.487 (9)
O(1)′···N(2)	2.711 (7)	C(1)–C(2)	1.508 (9)
O(1)′–C(3)	1.263 (7)	C(3)–C(4)	1.501 (9)
	Angles		
Cr′–Cr–Cl(1)	175.53 (6)	Cr–O(1)–C(3)′	119.6 (4)
–O(1)	87.1 (1)	Cr–O(2)–C(3)	122.9 (4)
–O(2)	85.0 (1)	Cr–O(3)–C(1)	122.6 (5)
–O(3)	84.6 (1)	Cr–O(4)–C(1)′	119.7 (4)
–O(4)	87.1 (1)	C(2)–N(1)···O(4)′	62.0 (6)
Cl(1)–Cr–O(1)	97.3 (1)	C(4)–N(2)···O(1)′	61.7 (6)
–O(2)	90.6 (1)	O(3)–C(1)–O(4)′	125.5 (6)
–O(3)	94.7 (1)	–C(2)	115.0 (6)
–O(4)	93.5 (1)	O(4)′–C(1)–C(2)	119.4 (6)
O(1)–Cr–O(2)	172.1 (2)	N(1)–C(2)–C(1)	111.4 (6)
–O(3)	89.4 (2)	O(1)′–C(3)–O(2)	125.4 (6)
–O(4)	90.7 (2)	–C(4)	119.9 (6)
O(2)–Cr–O(3)	90.1 (2)	O(2)–C(3)–C(4)	114.7 (6)
–O(4)	88.7 (2)	N(2)–C(4)–C(3)	111.6 (6)
O(3)–Cr–O(4)	171.7 (2)		

essentially copplanar orientation in each glycyl group. The NH_3^+ groups apparently participate in the formation of intramolecular hydrogen bonds to the O(1) and O(2) atoms of the bridging carboxyl groups as evidenced by O(1)···N(1) and O(2)···N(2) separations of 2.674 (8) and 2.701 (7) Å, respectively. The planar configuration in conjunction with intramolecular hydrogen-bond formation results in notable angular distortions about the carbon atoms in the glycine moieties. The bridging O–C–O groups have angles that appear normal with an average of 125.6 (6)°, but the four unique O–C–C angles are no longer equivalent and reflect the presence of the ammonium nitrogen atom. Thus, the O(1)–C(1)–C(2) and O(2)–C(3)–C(4) angles of 119.1 (6) and 119.1 (7)° are more obtuse by a factor of 5σ than the O(3)′–C(1)–C(2) and O(4)′–C(3)–C(4) angles of 114.4 (6) and 116.3 (7)°. Additionally, the two N–C–C angles that are both 110.4 (6)° are slightly distorted from the tetrahedral angle of 109.5°.

Although the hydrogen atoms of the glycine nitrogen and water oxygen atoms were not located, a number of short interatomic distances involving non-hydrogen atoms at less than 3.5 Å can be identified, which is suggestive of a tight web of hydrogen bonding throughout the crystal lattice. The Br(2) ion in the lattice has no contacts with either N(1) or N(2) of less than 3.5 Å, and only three contacts with the lattice oxygen atoms of the water molecules are in the 3.3–3.5 Å range. Figure 1A[22] displays the compact hydrogen-bonding network, and 14 probable contacts are listed in Tables IV and IVA.[22]

$Cr_2(O_2CCH_2NH_3)_4Cl_4 \cdot 3H_2O$ (2). Two formula weights are included in the contents of the unit cell of this molecule, with each molecule located on an inversion center at the midpoint of the Cr–Cr bond. Figure 2 provides a view of the $[Cr_2(O_2CCH_2NH_3)_4Cl_2]^{2+}$ cation with the atom-labeling scheme given. The inversional symmetry relates the primed atoms to unprimed ones. The crystal structure of **2** is isomorphous to the previously studied molybdenum analogue.[23] However, the bonding about the Cr_2^{4+} unit resembles that in other

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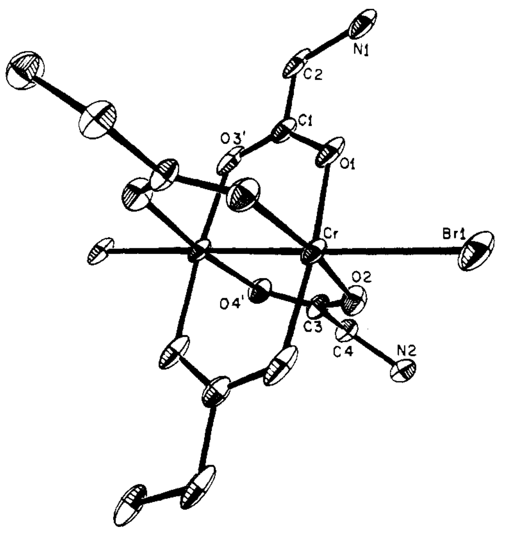

Figure 1. ORTEP plot of the $[Cr_2(O_2CCH_2NH_3)_4Br_2]^{2+}$ unit in **1**, with vibrational ellipsoids drawn at the 50% probability level. A crystallographic center of inversion is located at the midpoint of the Cr–Cr bond.

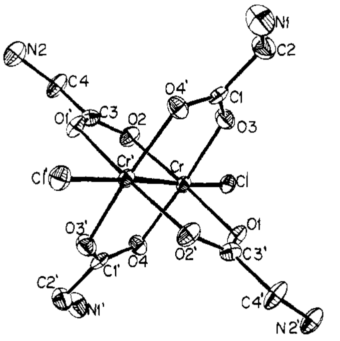

Figure 2. ORTEP drawing of the dinuclear $[Cr_2(O_2CCH_2NH_3)_4Cl_2]^{2+}$ unit in **2**, with thermal ellipsoids enclosing 50% of their electron density. The dinuclear molecule resides on a center of inversion that relates primed atoms to unprimed ones.

$Cr_2(O_2CR)_4L_2$ complexes.[3] The Cr–Cr bond length of 2.524 (1) Å is 0.011 Å longer than in **1**, and the axial Cl^- ions at 2.581 (1) Å from the Cr centers are 0.155 Å *closer* than the analogous Br^- ions in **1** and displaced to a greater extent off the Cr–Cr bond axis with a Cr′–Cr–Cl(1) angle of 175.53 (6)°. Four glycine oxygen atoms occupy equatorial positions about each Cr atom at an average distance of 2.028 (4) Å.

A description of the bonding in the two crystallographically unique glycyl residues in **2** follows that given for **1**. Two intramolecular hydrogen bonds represented by O(1)···N(2) and O(4)···N(1) separations of 2.711 (7) and 2.692 (7) Å, respectively, affect the bonding about the glycyl carbon atoms. The bridging O–C–O groups show an average 125.5 (6)° angle at the carbon atoms. Again, the four O–C–C angles are inequivalent with the more obtuse set, O(4)′–C(1)–C(2) and O(1)′–C(3)–C(4) that average 119.7 (6)°, located endocyclic to the four-membered ring comprised of the two glycyl carbon atoms and the hydrogen-bonded oxygen and nitrogen atoms. The exocyclic angles O(3)–C(1)–C(2) and O(2)–C(3)–C(4) have a mean value of 114.9 (6)°, which is less than that of the previous set by 8σ. A slight deviation away from the tetrahedral angle again is seen in the N–C–C angles that average 111.5 (6)°.

The shorter hydrogen-bonded contacts of the chloride ions in **2** compared to the bromide ions in **1** result in a slightly larger number of hydrogen-bonding interactions in **2**. On the basis of unit cell volumes, the average volume occupied by a non-hydrogen atom in **2** is 18.5 Å^3 while this value increases to 20.4 Å^3 in **1**. Figure IIA[22] clearly illustrates the alternating packing geometry of the Cr_2^{4+} molecules in **2** and highlights some prominent contacts between the nitrogen atoms of the glycyl ammonium groups and the oxygen atoms of the lattice water molecules. A listing of some 17 probable hydrogen-bonded contacts (2.79–3.36 Å) appears in Table VA.[22]

Discussion

The purple crystalline solids deposited upon addition of glycine to aqueous acid solution of chromous halides are shown by X-ray crystallography to consist of dinuclear chromium atoms bridged by four zwitterionic glycine molecules. The basic structural features of these chromium(II)–glycine compounds including the dinuclear formulation and the zwitterionic glycine groups were proposed correctly by Herzog and Kalies[18] who prepared **1** for the first time. The structural details presented here confirm those predictions.

A unique property of these glycine complexes of chromium (II) also noted by Herzog and Kalies[18] for **1** is their remarkable stability in air once isolated from solution. Previously it has been observed[3,24] that $Cr_2(mhp)_4$, where mhp is the anion of 2-hydroxy-6-methylpyridine, is stable toward atmospheric oxygen for several weeks making it one of the most stable chromium(II) compounds known. These $[Cr_2(O_2CCH_2NH_3)_4]^{4+}$ complexes appear to be *indefinitely* stable toward atmospheric oxygen in the solid state. Once the hydrated salts are isolated in crystalline form, there is no tendency toward dehydration at room temperature. The unique stability of these compounds can be attributed to the tight hydrogen-bonding networks (vide supra) that link the dinuclear cations to the halide ions and water molecules in the crystal lattice. These compounds may serve as a convenient entry point for further reaction chemistry involving Cr^{2+} species or spectroscopic studies.

Bonding in Zwitterionic Glycine Groups. For all amino acids including peptides that have been crystallized from solution, the crystal structures show the zwitterionic formula prevails in which the carboxylate proton has transferred in most cases to the amino group on the α-carbon atom.[25] When glycine adopts the zwitterionic $^-O_2CCH_2NH_3^+$ form,[26] the carboxyl moiety becomes an effective bidentate electron donor ligand poised for interaction with the acidic protons of the NH_3^+ group or with a dimetal fragment as found in various Mo_2^{4+} complexes[12,13,23] or the two Cr_2^{4+} complexes reported here. These structures invite a comparison of the effects of carboxyl group interactions on the bond distances and angles within the glycyl zwitterion. The pertinent dimensions are tabulated in Table VI.

The data displayed in Table VI show explicity the inflexibility of the zwitterionic glycine group regardless of the means of association of the carboxylate moiety with either acidic protons in the crystal lattice[26] or dimetal units of Cr(II) or Mo(II). The grand averages listed reveal that no interatomic dimension of the glycyl groups exceeds 3 esd's. This structural rigidity stems from the sp^2 hybridization of the carboxyl carbon atom combined with intramolecular hydrogen-bond formation between the NH_3^+ group and one of the two carboxyl oxygen atoms. Although this hydrogen bonding gives rise to additional bonding interactions to one of the two carboxyl oxygen atoms, the C–O distances do not reflect this difference and are once essentially independent of the intermolecular interations in accord with previous observations.[25] However, in the two unique O–C–C angles, denoted in Table VI by β and γ, the

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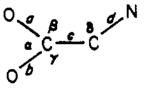
Table VI. Comparison of Dimensions in Free Glycine and Its Zwitterionic Complexes



compd	dimension[a]								ref
	a	*b*	*c*	*d*	α	β	γ	δ	
$^{-}O_2CCH_2NH_3^{+}$	1.250 (1)	1.251 (1)	1.526 (1)	1.476 (1)	125.45 (8)	117.46 (6)	117.09 (7)	111.85 (5)	24
$Cr_2(O_2CCH_2NH_3)_4Br_4\cdot4H_2O$	1.250 (7)	1.267 (8)	1.515 (9)	1.499 (8)	125.6 (6)	119.1 (7)	115.4 (7)	110.4 (6)	*b*
$Cr_2(O_2CCH_2NH_3)_4Cl_4\cdot3H_2O$	1.259 (8)	1.261 (7)	1.505 (9)	1.494 (9)	125.5 (6)	119.7 (6)	114.9 (6)	111.5 (6)	*b*
$Mo_2(O_2CCH_2NH_3)_4Cl_4\cdot3H_2O$[c]	1.259 (8)	1.268 (9)	1.52 (1)	1.49 (1)	124.2 (6)	120.5 (7)	115.4 (6)	110.6 (6)	23
$Mo_2(O_2CCH_2NH_3)_4Cl_4\cdot2^2/_3H_2O$	1.271 (9)	1.267 (9)	1.51 (1)	1.48 (1)	123.5 (6)	119.7 (7)	116.8 (7)	110.6 (7)	23
$Mo_2(O_2CCH_2NH_3)_4(SO_4)_2\cdot4H_2O$	1.243 (10)	1.281 (10)	1.510 (5)	1.486 (8)	124.0 (3)	120.8 (6)	115.1 (6)	110.0 (5)	12
cis-$Mo_2(O_2CCH_2NH_3)_2(NCS)_4\cdot H_2O$	1.24 (2)	1.25 (2)	1.53 (2)	1.45 (2)	125 (2)	119 (2)	117 (2)	108 (2)	13
grand average[d]	1.253 (11)	1.264 (11)	1.517 (9)	1.482 (16)	124.8 (8)	119.5 (11)	116.0 (10)	110.4 (12)	

[a] Bond distances in Å; angles given in deg. Equivalent dimensions have been averaged. [b] This work. [c] Isomorphous to the Cr analogue above. [d] The esd shown here represented the mean deviation from the mean.

Table VII. Some Representative Bond Lengths in Dichromium(II) Tetracarboxylates

compd	Cr–Cr, Å	Cr–L, Å	pK_a[a]	ref
$Cr_2(O_2CCF_3)_4(Et_2O)_2$	2.541 (1)	2.244 (3)	0.23	36
$Cr_4(O_2CCH_3)_4(OCH_2CH_2NMe_2)_4$	2.531 (2)	2.444 (5)[b]	4.75	41
$Cr_2(O_2CCH_2NH_3)_4Cl_4\cdot3H_2O$ (2)	2.524 (1)	2.581 (1)	2.34	this work
$Cr_2(O_2CCH_2NH_3)_4Br_4\cdot4H_2O$ (1)	2.513 (1)	2.736 (1)	2.34	this work
$(NH_4)_2[Cr_2(O_2CC_2H_5)_4(NCS)_2]$	2.467 (3)	2.249 (3)	4.87	42
$Cr_3(O_2CH)_6(H_2O)_2$[c]	2.451 (1)	2.224 (2)	3.75	36
$Cr_2(O_2CCH_3)_4(H_2O)_2$	2.362 (1)	2.272 (3)	4.75	28
$Cr_2(O_2CPh)_4(PhCO_2H)_2$	2.352 (3)	2.295 (7)	4.19	36
$(NH_4)_4[Cr_2(CO_3)_4(H_2O)_2]\cdot1.6H_2O$	2.214 (1)	2.300 (3)	10.25	37

[a] Value for carboxylic acid from which the bridging carboxylate is derived. [b] In this tetranuclear molecule only two cis acetate groups bridge each Cr–Cr bond, with the nitrogen atoms occupying equivalent axial sites. [c] The dinuclear unit has the form $Cr_2(O_2CH)_4(HCO_2^{-})_2$.

disparity caused by the presence of the amino nitrogen is apparent throughout the entire series, with the β angles averaging 119.5 ± 1.1° while the γ angles show a mean of only 116.0 ± 1.0°. These values are in excellent agreement with average angles found by Marsh and Donohue[25] of 118.0 and 116.4° for β and γ, respectively, in an extensive series of amino acid crystal structures. The data presented here serve to reinforce the concept that coordination of a dimetal unit to the carboxylate group leaves the remaining amino acid (or peptide) fragment free to adopt its uncomplexed configuration.[14]

The Quadruple Cr–Cr Bond. Since the first conceptualization 20 years ago of a quadruple bond between metal atoms[27] formed by d-orbital overlaps and the extension of this description to Cr_2^{4+} compounds,[28] a vast amount of theoretical[29–31] and experimental[3,32–34] work has appeared directed at achieving an understanding of the bonding in dichromium(II) compounds. The shallow potential energy curve for Cr_2^{4+} complexes leads to an extraordinary range of Cr–Cr distances varying from 1.828 (2)[35] to 2.541 (1) Å for $Cr_2(O_2CCF_3)_4(Et_2O)_2$.[36] The lower limit for compounds of the $Cr_2(O_2CR)_4L_2$ type is 2.214 (1) Å as found in $(NH_4)_4[Cr_2(CO_3)_4(H_2O)_2]\cdot1.6H_2O$,[37] and **1** and **2** belong to this group. Although theoretical studies are now able to predict qualitative correlations between Cr–Cr bond lengths and the donor strength of the bridging ligands,[31] quantitative detail is lacking in $Cr_2(O_2CR)_4L_2$ compounds and empirical relationships have been sought.

Among metal–metal multiply bonded compounds of the type $M_2(O_2CR)_4L_2$ for which a number of compounds having R groups with varying inductive effects have been prepared and structurally characterized, the dimolybdenum(II) tetracarboxylates are found to be relatively insensitive to the nature of the R group.[38] For $Mo_2(O_2CCH_3)_4$[39] and $Mo_2(O_2CCF_3)_4$,[40] the Mo–Mo distances of 2.0934 (8) and 2.090 (4) Å are practically identical. The $CH_2NH_3^{+}$ substituent in $Mo_2(O_2CCH_2NH_3)_4Cl_4\cdot3H_2O$,[23] the isomorphous molybdenum analogue of **2**, results in a slight increase in the Mo–Mo bond to 2.112 (1) Å, but this increase may be attributed to crystal-packing forces or the presence of axial Cl^{-} ions. In contrast to the situation just described for Mo_2^{4+}, the dichromium(II) tetracarboxylates are remarkably *sensitive* to both the R group substituent and the presence of axial ligands L.[3,32] A loose correlation[37] has been found to exist between the Cr–Cr bond length and the donor strength of the bridging carboxylate group as gauged by the pK_a value of the corresponding acid. Some representative data are collected in Table VII.

As can be seen in Table VII, a decrease in the Cr–Cr distance roughly correlates with an increase in pK_a value (or decrease in pK_b). The highly electron-withdrawing effect of the CF_3 group in $Cr_2(O_2CCF_3)_4(Et_2O)_2$ is evidenced by the longest known Cr–Cr bond length to date. The $[Cr_2(O_2CCH_2NH_3)_4]^{4+}$ compounds **1** and **2** in this study have Cr–Cr distances within 0.034 Å of this value, and clearly this

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can be attributed in part to the electron-withdrawing character of the $CH_2NH_3^+$ group. The seemingly anomalous Cr–Cr bond length in the recently reported tetranuclear $Cr_4(O_2CCH_3)_4(OCH_2CH_2NMe_2)_4$ compound[41] can be explained by the absence of two of the bridging acetate groups in each of the two dinuclear units. The influence of the axial ligands on the Cr–Cr bond length cannot be dismissed, but the effects of the halide ligands in **1** and **2** are unknown since these are the first structurally characterized $Cr_2(O_2CR)_4L_2$ compounds found with other than nitrogen or oxygen axial donor atoms.

The dinuclear structures found for **1** and **2** afford a partial explanation of the magnetic properties reported by Herzog and Kalies for **1**.[18] Thus, the depressed magnetic moment in **1** of 0.79 μ_B/Cr most likely results from a combination of superexchange interactions across the $[Cr_2(O_2CCH_2NH_3)_4]^{4+}$ unit combined with some direct exchange propagated by means of the Cr–Cr bond. Since previous work has suggested the presence of some Cr^{3+} impurities in $Cr_2(O_2CR)_4L_2$ compounds,[43] a more detailed study using variable-temperature magnetic susceptibility measurements is needed to unravel antiferromagnetic and paramagnetic impurity contributions in $Cr_2(O_2CCH_2NH_3)_4Br_4{\cdot}4H_2O$. The solution magnetic moment observed for **1** of 4.83 μ_B is close to the spin-only value of 4.90 μ_B for four unpaired electrons in high-spin Cr^{2+}. This suggests that the dinuclear units do not remain intact in solution. Support for this suggestion is derived from a recent structure containing mononuclear square-planar Cr^{2+} ions coordinated by monodentate trifluoroacetate ligands.[44] This tendency toward facile $Cr\overset{4}{-}Cr$ bond scission in solution is in marked contrast to analogous Mo_2^{4+} complexes where simple substitution reactions leave the $Mo\overset{4}{-}Mo$ bond intact.

Acknowledgment. We are grateful for financial support by the Bat-Sheba Foundation (to A.B.).

Registry No. **1**, 92126-99-3; **2**, 92127-00-9; Cr, 7440-47-3.

Supplementary Material Available: Tables IIA and IIIA (anisotropic thermal parameters for $Cr_2(O_2CCH_2NH_3)_4Br_4{\cdot}4H_2O$ (**1**) and $Cr_2(O_2CCH_2NH_3)_4Cl_4{\cdot}3H_2O$ (**2**), respectively), Tables IVA and VA (hydrogen-bonded contacts in **1** and **2**, respectively), listings of observed and calculated structure factor amplitudes for **1** and **2**, and figures of unit cell contents for **1** and **2** (23 pages). Ordering information is given on any current masthead page.

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3,3′,4,4′-Tetramethyl-1,1′-diphosphaferrocene (DPF): Template Ligand for the Formation of Polymetallic Complexes

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The donor properties of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (DPF) were investigated by preparing a series of 13 complexes of this ligand. Reaction of DPF with $(THF)M(CO)_5$ (M = Cr, Mo, W) gives the monometallic monoligate complexes $(DPF)M(CO)_5$ from which the bimetallic biligate $(DPF)[M(CO)_5]_2$ (M = Cr, Mo, W) and $M(CO)_5(DPF)M'(CO)_5$ (M = Cr, M′ = Mo, W; M = Mo, M′ = W) were prepared. Similarly, DPF and $Mn_2(CO)_{10}$ produce $(DPF)Mn_2(CO)_9$ and $(DPF)[Mn_2(CO)_9]_2$. Reaction of $RuCl_3{\cdot}3H_2O$ with DPF in refluxing methanol produces *trans*-$(DPF)_4RuCl_2$ while reaction of $(PPh_3)_3RuCl_2$ with DPF produces the bimetallic biligate $[(PPh_3)Ru(DPF)(\mu\text{-}Cl)Cl]_2$ containing both bridging and terminal chlorides. These complexes have been characterized by elemental analyses, infrared, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, and mass spectrometry. The ligand DPF is shown to be a better donor than PPh_3 toward ruthenium(II) by chemical reactivity studies. Cotton–Kraihanzel force constants for the $(DPF)M(CO)_5$ complexes suggest that DPF is a better σ donor and much better π acceptor than 1-phenyl-3,4-dimethylphosphole. The crystal structure of $[(PPh_3)Ru(DPF)(\mu\text{-}Cl)Cl]_2$ has been determined by three-dimensional X-ray diffraction techniques. The molecule crystallizes in the triclinic space group $P\bar{1}$ in a unit cell of dimensions a = 12.566 (4) Å, b = 13.100 (4) Å, c = 12.202 (4) Å, α = 110.58 (2)°, β = 104.24 (2)°, γ = 66.08 (2)°, and ρ_{calcd} = 1.62 g cm^{-3} with $Z = 1$. Refinement converged to R = 0.069 with 3814 independent reflections. The structure indicates that the phospholyl rings remain fully aromatic in the complex. The three C–C bond lengths are almost equal, with a mean value of 1.415 (4) Å. The two ruthenium centers are six-coordinate with asymmetric chloride bridges, terminal chlorides, terminal PPh_3, and two bridging DPF ligands. The DPF phosphorus atoms are eclipsed in contrast to free DPF where phosphorus eclipses the β-carbon. The Ru–P(DPF) distances are short (2.2935 (4) Å, average), which is shorter than the Ru–P(PPh_3) distances (2.311 (4) Å). The two triphenylphosphines occupy anti positions (one on each ruthenium) such that the two sides of the phospholyl rings are not in equivalent environments. This inequivalence is manifested in the ^1H and $^{13}C\{^1H\}$ NMR spectra of this compound.

Introduction

Polymetallic complexes are receiving considerable attention for several reasons.[2] Paramount among these is the notion that metals held proximate may exhibit cooperativity in both their chemical and physical properties. This notion portends useful applications for polymetallic complexes in such areas as catalysis,[3] conducting materials,[2] and enzyme models.[4] Most of the polymetallic complexes synthesized to date contain metal–metal bonds[5] or bridging ligands such as halides,

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