

first report of $\text{Rh}_2(\text{OAc})_4(\text{Me}_2\text{SO})_2$ in 1963 by Johnson, Hunt, and Neumann.²⁰ These authors proposed that Me_2SO coordinated through the sulfur atom on the basis of the orange color of the adduct (oxygen-ligated adducts were recognized to be green to blue-green) and the position of the S-O stretching frequency (1086 cm^{-1}) in the infrared spectrum. The latter observation was known²⁶ to be diagnostic of metal-sulfur bonding since the S-O stretching frequency exceeded that of the free ligand (1055 cm^{-1}). These stretching frequencies are consistent with the S-O distances as determined by X-ray crystallography. In Me_2SO itself the S-O bond length is $1.513(5)\text{ \AA}$ ²⁷ whereas in $\text{Rh}_2(\text{OAc})_4(\text{Me}_2\text{SO})_2$ the distance has decreased to $1.477(5)\text{ \AA}$. In $\text{PdCl}_2(\text{Me}_2\text{SO})_2$, for example, where Pd-S bonding has been found, the S-O distance is $1.475(5)\text{ \AA}$ ²⁸ ($\nu(\text{S-O stretch}) = 1116\text{ cm}^{-1}$). Very strong bonding to the sulfur as in the $(\text{CH}_3)_3\text{SO}^+$ ion leads to a still shorter S-O distance^{29,30} ($1.45(1)\text{ \AA}$) and a higher

S-O stretching frequency²⁶ (1233 cm^{-1}), as expected.

The Rh-S distance of $2.451(1)\text{ \AA}$ in **3** clearly demonstrates the influence of the trans effect of the Rh-Rh bond on the bond length. Normal Rh-S bond lengths are in the range $2.23\text{--}2.26\text{ \AA}$ as found in $\text{Rh}_2(\text{OSCCCH}_3)_4(\text{CH}_3\text{CSOH})_2$ ¹⁹ and *fac*- $\text{RhCl}_3(\text{Me}_2\text{SO})_3$.³¹ The latter complex with Rh(III) has only two Me_2SO molecules coordinating through the sulfur atom. The Rh-S distance in $\text{Rh}_2(\text{OAc})_4(\text{Me}_2\text{SO})_2$ (**2**) is shorter by nearly 0.07 \AA than in the THT adduct **3** and this would point to the presence of greater π back-bonding interactions in **2** as has been suggested previously from evaluation of thermodynamic data.²⁵

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Supplementary Material Available: Tables of observed and calculated structure factors for the three compounds (25 pages). Ordering information is given on any current masthead page.

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Pyridine and Pyrazine Adducts of Tetrakis(acetato)dichromium

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Pyridine and pyrazine form 2:1 and 1:1 adducts, respectively, with $\text{Cr}_2(\text{OAc})_4$ which have been characterized by X-ray crystallography. The structures are isomorphous to those of the corresponding copper(II) complexes. Crystals of $\text{Cr}_2(\text{OAc})_4(\text{py})_2$ (**1**) are orthorhombic and belong to space group *Pbca* with four molecules in a unit cell of dimensions $a = 13.055(2)\text{ \AA}$, $b = 8.645(1)\text{ \AA}$, $c = 19.560(3)\text{ \AA}$, and $V = 2207.5(6)\text{ \AA}^3$. The structure was refined with 891 reflections having $I > 3\sigma(I)$ to final discrepancy indices of $R_1 = 0.060$ and $R_2 = 0.081$. The structure consists of centrosymmetric formula units with a Cr-Cr bond length of $2.369(2)\text{ \AA}$ and a Cr-N bond length of $2.335(5)\text{ \AA}$. The pyrazine (pyz) adduct, $\text{Cr}_2(\text{OAc})_4(\text{pyz})_2$ (**2**), crystallizes in the space group *C2/m* with $a = 7.979(2)\text{ \AA}$, $b = 14.350(4)\text{ \AA}$, $c = 7.376(2)\text{ \AA}$, $\beta = 101.78(2)^\circ$, $V = 826.7(4)\text{ \AA}^3$, and $Z = 2$. The structure was solved by using 365 reflections with $I > 2\sigma(I)$ to give final residuals of $R_1 = 0.065$ and $R_2 = 0.079$. The Cr-Cr bond length in the $\text{Cr}_2(\text{OAc})_4$ units is $2.295(5)\text{ \AA}$ and these centrosymmetric units are linked into linear chains by the pyrazine molecules with C-N bond lengths of $2.31(1)\text{ \AA}$.

Introduction

Dichromium(II) complexes are of interest because of the extraordinary variation in the Cr-Cr bond length.¹ The range extends from $1.828(2)\text{ \AA}$ in tetrakis(2-methoxy-5-methylphenyl)dichromium(II)² to $2.541(1)\text{ \AA}$ in $\text{Cr}_2(\text{O}_2\text{CCF}_3)_4(\text{Et}_2\text{O})_2$.³ The distribution of the Cr-Cr bond lengths has been bimodal with the carboxylates constituting an upper range ($2.28\text{--}2.54\text{ \AA}$) and most of the others falling between the value of 1.98 \AA in $[\text{Cr}_2(\text{CH}_3)_8]^{4+}$ and the aforementioned 1.828 \AA . The existence of Cr-Cr bonds of order 4 is universally accepted for the species in the lower range, but controversy⁵ has arisen

concerning those in the upper range. However, the existence of weak quadruple bonds in the carboxylato compounds has been supported by the results of SCF-X α -SW calculations⁶ and Hartree-Fock calculations in which at least partial account of electron correlation has been included.⁷ The latter calculations suggest that the curve of energy vs. Cr-Cr distance for a $\text{Cr}_2(\text{O}_2\text{CR})_4$ system is very shallow and thus, at least in part, allow us to understand the extreme sensitivity of Cr-Cr bond length to the identities of R and L in the $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$ compounds.³ However, no neat, unambiguous relationships have yet been found and consequently efforts have continued

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Table I. Crystallographic Data

parameter	$\text{Cr}_2(\text{OAc})_4(\text{py})_2$ (1)	$\text{Cr}_2(\text{OAc})_4(\text{pyz})$ (2)
space group	<i>Pbca</i>	<i>C2/m</i>
<i>a</i> , Å	13.055 (2)	7.979 (2)
<i>b</i> , Å	8.645 (1)	14.350 (4)
<i>c</i> , Å	19.560 (3)	7.376 (2)
β , deg	90.0	101.78 (2)
<i>V</i> , Å ³	2207.5 (6)	826.7 (4)
d_{calcd} , g/cm ³	1.50	1.69
<i>Z</i>	4	2
fw	498.38	420.26
cryst size, mm	0.3 × 0.3 × 0.2	0.2 × 0.2 × 0.1
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	10.728	14.132
range 2 θ , deg	4–45	5–45
no. unique data	1085	474
no. data, $F_o^2 > 3\sigma(F_o^2)$	891	365 ^a
no. variables	91	45
R_1^b	0.060	0.065
R_2^b	0.081	0.079
esd ^b	1.689	1.458
largest peak, ^c e/Å ³	0.67	1.48

^a $F_o^2 > 2\sigma(F_o^2)$. ^b R_1, R_2 , and esd are defined the usual way; see for example ref 16. ^c Largest peaks in the final difference Fourier maps.

toward gaining a better understanding of the electronic structure and bonding in these compounds.^{8,9}

This paper reports the preparation and crystal structures for the pyridine (py) and pyrazine (pyz) adducts of $\text{Cr}_2(\text{OAc})_4$. A previous attempt to obtain the pyridine complex in crystalline form was unsuccessful,¹⁰ and hence, the preparation of $\text{Cr}_2(\text{OAc})_4(\text{py})_2$ (**1**) is reported here for the first time. The bifunctional pyrazine ligand was intended to provide a continuous π -bonded pathway between metal ions. It has been previously employed in studies of electron exchange¹¹ and transfer¹² processes. A novel linear-chain complex has been prepared with $\text{Cu}_2(\text{OAc})_4$ units linked together by pyrazine ligands in order to study the effects of intermolecular exchange.^{13,14} The analogous chromium(II) complex, namely, $\text{Cr}_2(\text{OAc})_4(\text{pyz})$ (**2**), has now been prepared and its structure determined so as to ascertain the effects of the axial bridging ligand and linear-chain arrangement on the Cr–Cr bond length.

Experimental Section

Compound Preparation. All reagents were degassed before use and manipulations were performed under an argon atmosphere. The hydrated and anhydrous forms of chromium acetate were prepared by using a literature method.¹⁵

$\text{Cr}_2(\text{OAc})_4(\text{py})_2$ (**1**) was prepared from a saturated aqueous solution of $\text{Cr}_2(\text{OAc})_4(\text{H}_2\text{O})$ which had been filtered into a Schlenk tube. Neat pyridine was gently layered on top of the aqueous solution. Red prismatic crystals began to grow after a few hours and attained their maximum size within 24 h.

$\text{Cr}_2(\text{OAc})_4(\text{pyz})$ (**2**) was isolated as an orange microcrystalline solid by mixing equimolar THF solutions of $\text{Cr}_2(\text{OAc})_4$ (prefiltered) and

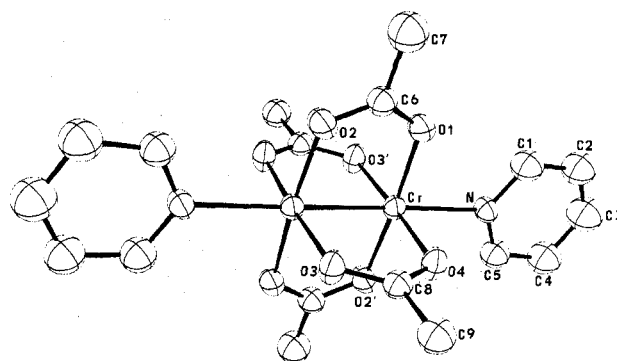


Figure 1. ORTEP drawing of $\text{Cr}_2(\text{OAc})_4(\text{py})_2$, α form (**1**), with thermal ellipsoids drawn at the 50% probability level. A crystallographic center of inversion is located at the midpoint of the Cr–Cr bond.

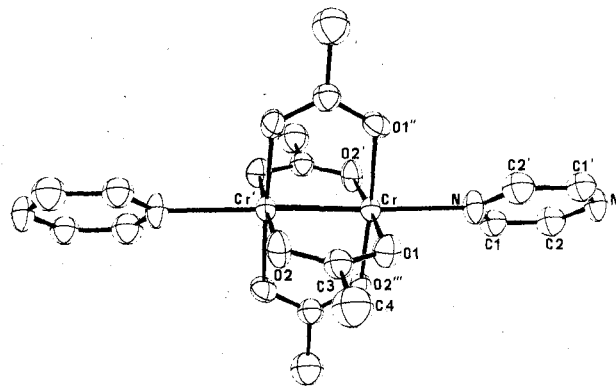


Figure 2. ORTEP plotting of a segment of the linear chains in $\text{Cr}_2(\text{OAc})_4(\text{pyz})$ (**2**) with 50% probability ellipsoids. Primed atoms are related to unprimed ones by inversion. Doubly and triply primed atoms are related to unprimed and singly primed ones, respectively, by a mirror plane.

pyrazine. Crystals were obtained by using a fritted U-tube. A filtered $\text{Cr}_2(\text{OAc})_4$ -THF solution was placed on one side of the U-tube, and on the other side a few crystals of pyrazine were added (approximately a stoichiometric amount) followed by enough THF to equalize the hydrostatic pressures on both sides. After 2–3 days, reddish orange crystals formed within the $\text{Cr}_2(\text{OAc})_4$ -THF solution.

X-ray Crystallography. Collection of Data. Crystals of both compounds were examined under a layer of degassed mineral oil. A red prism of **1** was mounted on a glass fiber and coated with a layer of epoxy cement. A crystal of **2** was embedded in epoxy cement in a glass capillary.

Data for both compounds were collected at $21 \pm 2^\circ \text{C}$ on a Syntex P1 autodiffractometer using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) with a graphite crystal monochromator in the incident beam. The general procedures for centering, indexing, and data collection have been given before.¹⁶ Unit cell constants for both crystals were obtained by a least-squares fitting of the setting angles for 15 reflections in the range $15^\circ < 2\theta < 28^\circ$. Lorentz and polarization corrections were applied to the data¹⁷ but no absorption corrections were made. A summary of the final cell parameters and details pertinent to the data collection and refinement are presented in Table I for compounds **1** and **2**.

Solution and Refinement of the Structures.¹⁷ An examination of the cell constants for both compounds revealed that each one was isomorphous with its copper analogue for each of which the structure had been previously determined.^{14,18} Refinement of $\text{Cr}_2(\text{OAc})_4(\text{py})_2$ was begun by using the atomic parameters for the copper(II) ana-

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $\text{Cr}_2(\text{OAc})_4(\text{py})_2$, α Form (1)^a

atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	0.0296 (1)	0.0668 (1)	0.04905 (6)	2.85 (5)	2.03 (5)	1.93 (4)	0.04 (6)	-0.02 (6)	-0.14 (5)
O(1)	0.1146 (5)	-0.0628 (7)	-0.0845 (3)	3.2 (3)	3.4 (3)	2.4 (2)	-0.4 (3)	0.3 (2)	-0.6 (2)
O(2)	0.1710 (5)	0.0607 (7)	0.0074 (3)	3.2 (3)	3.9 (3)	2.5 (2)	-0.2 (3)	0.3 (2)	-0.6 (2)
O(3)	0.0570 (5)	-0.1391 (6)	0.0931 (3)	4.6 (3)	2.1 (2)	2.5 (2)	0.1 (2)	-0.5 (2)	-0.1 (2)
O(4)	-0.0018 (5)	0.2634 (7)	-0.0008 (3)	4.7 (3)	2.2 (2)	2.4 (2)	0.0 (2)	-0.6 (2)	-0.3 (2)
N	0.0902 (6)	0.2023 (8)	0.1440 (3)	4.1 (4)	2.7 (3)	2.1 (3)	-0.1 (3)	0.4 (3)	-0.3 (3)

atom	<i>x</i>	<i>y</i>	<i>z</i>	$B, \text{\AA}^2$	atom	<i>x</i>	<i>y</i>	<i>z</i>	$B, \text{\AA}^2$
C(1)	0.0279 (8)	0.229 (1)	0.1968 (5)	4.2 (2)	C(6)	0.1849 (7)	-0.003 (1)	-0.0491 (4)	2.9 (2)
C(2)	0.0629 (9)	0.313 (1)	0.2542 (5)	4.9 (2)	C(7)	0.2951 (9)	-0.012 (1)	-0.0751 (5)	4.7 (2)
C(3)	0.1610 (9)	0.367 (1)	0.2549 (6)	5.6 (3)	C(8)	0.0385 (7)	-0.262 (1)	0.0604 (4)	2.5 (2)
C(4)	0.2270 (9)	0.341 (1)	0.1990 (5)	5.0 (2)	C(9)	0.0623 (7)	-0.415 (1)	0.0936 (5)	3.8 (2)
C(5)	0.1853 (7)	0.255 (1)	0.1439 (5)	3.7 (2)					

^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 III. Positional and Thermal Parameters and Their Estimated Standard Deviations for $\text{Cr}_2(\text{OAc})_4(\text{pyz})_2$ (2)^a

atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	0.1222 (3)	0.0 ^b	0.1132 (4)	1.91 (8)	2.58 (9)	1.79 (8)	0.0 ^b	0.04 (7)	0.0 ^b
O(1)	0.0165 (8)	-0.1003 (5)	0.2436 (9)	3.2 (3)	3.4 (4)	2.5 (3)	-0.3 (3)	0.7 (3)	0.9 (3)
O(2)	0.2201 (8)	0.0979 (5)	-0.0292 (9)	2.3 (3)	4.3 (4)	2.9 (3)	-0.9 (3)	-0.2 (3)	0.5 (3)
N	0.360 (1)	0.0 ^b	0.353 (2)	1.8 (5)	5.2 (7)	2.4 (6)	0.0 ^b	0.3 (4)	0.0 ^b

atom	<i>x</i>	<i>y</i>	<i>z</i>	$B, \text{\AA}^2$	atom	<i>x</i>	<i>y</i>	<i>z</i>	$B, \text{\AA}^2$
C(1)	0.522 (2)	0.0 ^b	0.328 (2)	3.3 (3)	C(3)	-0.131 (1)	-0.1295 (8)	0.176 (1)	2.9 (2)
C(2)	0.658 (2)	0.0 ^b	0.473 (2)	4.0 (4)	C(4)	-0.202 (2)	-0.2096 (10)	0.273 (2)	4.8 (3)

^a The form of the anisotropic thermal parameter is $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. ^b Value required by the atom position.

Table IV. Bond Distances (Å) and Angles (Deg) for $\text{Cr}_2(\text{OAc})_4(\text{py})_2$, α Form (1)

Distances			
Cr-Cr'	2.369 (2)	C(2)-C(3)	1.36 (1)
Cr-O(1)	2.007 (5)	C(3)-C(4)	1.41 (1)
Cr-O(2')	2.018 (5)	C(4)-C(5)	1.42 (1)
Cr-O(3')	2.009 (4)	O(1)-C(6)	1.259 (8)
Cr-O(4)	2.002 (5)	O(2)-C(6)	1.249 (8)
Cr-N	2.335 (5)	O(3)-C(8)	1.265 (8)
N-C(1)	1.33 (1)	O(4)-C(8)	1.260 (8)
N-C(5)	1.32 (1)	C(6)-C(7)	1.53 (1)
C(1)-C(2)	1.41 (1)	C(8)-C(9)	1.51 (1)

Angles			
Cr'-Cr-O(1)	88.0 (1)	Cr'-O(3)-C(8)	119.6 (4)
Cr'-Cr-O(2')	87.6 (1)	Cr-O(4)-C(8)	121.4 (4)
Cr'-Cr-O(3')	88.5 (1)	Cr-N-C(1)	119.7 (5)
Cr'-Cr-O(4)	87.3 (1)	Cr-N-C(5)	119.3 (5)
Cr'-Cr-N	178.6 (2)	C(1)-N-C(5)	120.9 (7)
O(1)-Cr-O(2')	175.6 (2)	N-C(1)-C(2)	120.5 (8)
O(1)-Cr-O(3')	90.2 (2)	C(1)-C(2)-C(3)	119.1 (9)
O(1)-Cr-O(4)	89.5 (2)	C(2)-C(3)-C(4)	120.9 (9)
O(1)-Cr-N	93.0 (2)	C(3)-C(4)-C(5)	115.8 (8)
O(2')-Cr-O(3')	89.3 (2)	N-C(5)-C(4)	122.7 (7)
O(2')-Cr-O(4)	90.7 (2)	O(1)-C(6)-O(2)	124.1 (7)
O(2')-Cr-N	91.4 (2)	O(1)-C(6)-C(7)	118.9 (6)
O(3')-Cr-O(4)	175.8 (2)	O(2)-C(6)-C(7)	116.9 (7)
O(3')-Cr-N	92.5 (2)	O(3)-C(8)-O(4)	123.2 (6)
O(4)-Cr-N	91.8 (2)	O(3)-C(8)-C(9)	118.8 (6)
Cr-O(1)-C(6)	120.1 (4)	O(4)-C(8)-C(9)	118.0 (6)
Cr'-O(2)-C(6)	120.1 (5)		

logue¹⁸ (orthorhombic α form). Subsequent refinement of all 15 atom positions with isotropic temperature factors followed by three cycles of least-squares refinement with anisotropic temperature factors for all noncarbon atoms led to the final residuals reported in Table I. The atomic parameters for the 298 K structure of $\text{Cu}_2(\text{OAc})_4(\text{pyz})_2$ ¹⁴ were used as input for the starting positions for the eight nonhydrogen atoms in $\text{Cr}_2(\text{OAc})_4(\text{pyz})_2$. The refinement for **2** converged with anisotropic thermal parameters for all noncarbon atoms to the values given in Table I. Hydrogen atoms were omitted from both structures. The final difference Fourier maps yielded no peaks of structural significance. Tables of observed and calculated structure factors are available as supplementary material.

Table V. Bond Distances (Å) and Angles (Deg) for $\text{Cr}_2(\text{OAc})_4(\text{pyz})_2$ (2)

Distances			
Cr-Cr'	2.295 (5)	N'-C(2)	1.32 (2)
Cr-O(1)	2.010 (6)	O(1)-C(3)	1.25 (1)
Cr-O(2')	2.006 (7)	O(2)-C(3)	1.25 (1)
Cr-N	2.314 (10)	C(1)-C(2)	1.36 (2)
N-C(1)	1.34 (2)	C(3)-C(4)	1.52 (1)

Angles			
Cr'-Cr-O(1)	88.3 (2)	Cr'-O(2)-C(3)	119.6 (6)
Cr'-Cr-O(2')	89.0 (2)	Cr-N-C(1)	123.6 (9)
Cr'-Cr-N	177.0 (4)	Cr-N-C(2')	120.6 (9)
O(1)-Cr-O(1'')	91.5 (4)	C(1)-N-C(2')	116 (1)
O(1)-Cr-O(2')	177.0 (3)	N-C(1)-C(2)	122 (1)
O(1)-Cr-O(2'')	89.7 (2)	C(1)-C(2)-N'	122 (1)
O(1)-Cr-N	89.6 (3)	O(1)-C(3)-O(2)	122.8 (9)
O(2')-Cr-O(2'')	88.9 (4)	O(1)-C(3)-C(4)	118.5 (9)
O(2')-Cr-N	93.2 (3)	O(2)-C(3)-C(4)	118.7 (9)
Cr-O(1)-C(3)	120.2 (6)		

Results and Discussion

The positional and thermal parameters for **1** and **2** are given in Tables II and III, while the bond distances and angles for the two structures appear in Tables IV and V. Figure 1 presents a view of $\text{Cr}_2(\text{OAc})_4(\text{py})_2$ and defines the atom numbering scheme used in Tables II and IV. A portion of the linear chains in $\text{Cr}_2(\text{OAc})_4(\text{pyz})_2$ is shown in Figure 2 with the atom labeling scheme as employed in Tables III and V.

The structure of $\text{Cr}_2(\text{OAc})_4(\text{py})_2$ is centrosymmetric with a Cr-Cr bond distance of 2.369 (2) Å and axially bound pyridine ligands at a distance of 2.335 (5) Å from each Cr atom. The structure closely resembles that of its copper(II) analogue¹⁸ to which it is isomorphous, but the Cr atoms display their own coordination preferences. For example, the copper(II) complex has a M-M separation which is nearly 0.3 Å greater (2.645 (3) Å) than the chromium(II) one and a much shorter axial M-N distance of 2.186 (8) Å. The metal-carboxylate oxygen distances average 2.009 (5) Å for the Cr compound but only 1.955 (8) Å for the Cu complex. The difference in metal-metal separation results in more acute

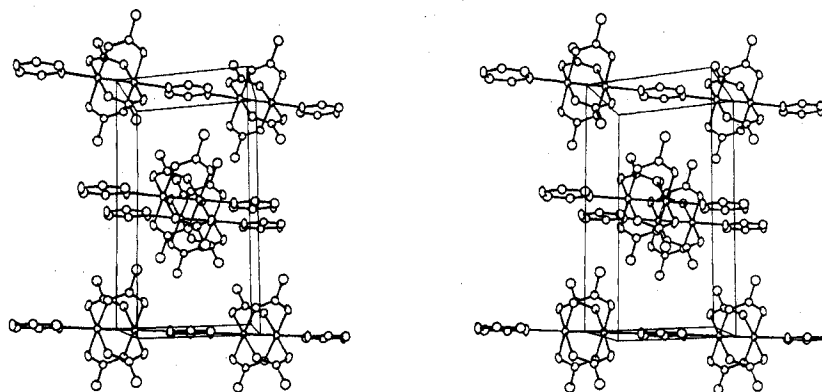


Figure 3. Stereoview of the linear chains within the unit cell of $\text{Cr}_2(\text{OAc})_4(\text{pyz})$ (**2**) with vibrational ellipsoids drawn at the 20% probability level. The view is down the c axis with the a axis horizontal and the b axis vertical.

M-M-O angles in the copper(II) compound ($83.7(4)^\circ$) than in the chromium(II) one ($87.8(1)^\circ$) although both compounds show nearly the same O-C-O angles ($123.5 \pm 0.1^\circ$, average).

As noted before,¹⁰ the Cr-Cr and Cr-L distances show the largest variations among the structural parameters for complexes of the general formula $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$. Two complexes which very closely resemble $\text{Cr}_2(\text{OAc})_4(\text{py})_2$ are $\text{Cr}_2(\text{OAc})_4(\text{pip})_2$ ¹⁰ (pip = piperidine, $\text{C}_5\text{H}_{11}\text{N}$) and $\text{Cr}_2(\text{O}_2\text{CH})_4(\text{py})_2$.³ The piperidine adduct has a shorter Cr-Cr bond length ($2.342(2) \text{ \AA}$) in accord with the greater basicity of piperidine ($\text{p}K_b = 2.88$) compared to pyridine ($\text{p}K_b = 8.75$). The piperidine complex, however, has a Cr-N bond length of $2.338(7) \text{ \AA}$ which is nearly identical with the corresponding value in **1**. The formate complex with a Cr-Cr bond length of $2.408(1) \text{ \AA}$ demonstrates that the Cr-Cr distance is much more sensitive to the nature of the bridging ligands than those in the axial position.

The bifunctional pyrazine ligand forms a 1:1 complex with $\text{Cr}_2(\text{OAc})_4$ linking the dichromium units into slightly zig-zagging chains with a Cr-N distance of $2.314(10) \text{ \AA}$ and a Cr'-Cr-N angle of $177.0(4)^\circ$. Four such chains pass through each unit cell in the arrangement depicted in Figure 3. The Cr-Cr quadruple bond has a surprisingly short length of $2.295(5) \text{ \AA}$. Crystallographic centers of inversion are located at the midpoints of the Cr-Cr bonds and at the centers of the pyrazine ligands. The Cr, N, C(1), and C(2) atoms are located on $(x, 0, z)$ positions which comprise a mirror plane that bisects the bridging acetate groups. Consequently, there is only one crystallographically distinct acetate group in the complex, the other three being produced by the inversion and mirror operations. Figure 3 clearly shows the pyrazine ligands situated parallel to each other on ac mirror planes and the packing geometry of the $\text{Cr}_2(\text{OAc})_4$ units. No unusual distances and angles within the acetate and pyrazine ligands are found.

A comparison of the structural parameters in **2** to those in $\text{Cu}_2(\text{OAc})_4(\text{pyz})$ ¹⁴ reveals that again the principal differences between the two complexes arise from the differences in the M-M separation and M-N and M-O bond distances. The Cu-Cu separation is $2.583(1) \text{ \AA}$ and the nearly 0.3 \AA increase

in M-M distance over that of the chromium compound results in a more acute M-M-O angle ($84.7(1)^\circ$ vs. $88.6(2)^\circ$ for Cr) and a greater O-C-O angle ($125.3(6)$ vs. $122.8(9)^\circ$).

The Cr-Cr distance in **2** is among the shortest to be reported for a dichromium carboxylate-bridged complex (cf. $2.283(2) \text{ \AA}$ in $\text{Cr}_2(9\text{-anthracenecarboxylate})_4\text{DME}$ ³ and $2.288(1) \text{ \AA}$ in $\text{Cr}_2(\text{OAc})_4$ ¹⁹). The pyridine (**2**) and piperidine¹⁰ adducts of $\text{Cr}_2(\text{OAc})_4$ have longer Cr-Cr distances consistent with the much greater basicity of these ligands compared to pyrazine ($\text{p}K_b = 13.35$). However, in $\text{Cr}_2(\text{OAc})_4(\text{H}_2\text{O})_2$, the Cr-Cr bond length of $2.362(1) \text{ \AA}$ ²⁰ clearly does not reflect the weak basicity of the aquo ligand when compared to these nitrogen-donor adducts. The pyrazine complex presents a more compact packing arrangement due to the 1:1 stoichiometry (cf. calculated densities in **1** and **2**) of $\text{Cr}_2(\text{OAc})_4$ to axial ligand. Packing forces have been suggested before¹⁰ as an effect which precludes a simple correlation between Cr-Cr and Cr-axial ligand bond lengths. Some support for these intermolecular effects on the M-M separation comes from the structure of $\text{Cu}_2(\text{OAc})_4(\text{pyz})$ which shows that despite the absence of metal-metal bonding, the Cu-Cu separation is the shortest distance yet discovered for a copper(II) carboxylate. A complete explanation of the bonding in $\text{Cr}_2(\text{O}_2\text{CR})_4\text{L}_2$ compounds will require an accurate description of the electronic structure which recent theoretical calculations are only beginning to provide.^{8,9}

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Registry No. **1**, 66197-70-4; **2**, 72186-99-3.

Supplementary Material Available: Table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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