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Structural and Magnetic Characterization of Di-μ-hydroxo-bis[bis(1,10-phenanthroline)chromium(III)] Iodide Tetrahydrate

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The crystal and molecular structure of di-μ-hydroxo-bis[bis(1,10-phenanthroline)chromium(III)] iodide tetrahydrate, $[Cr(phen)_2OH]_2I_4 \cdot 4H_2O$, has been determined from three-dimensional counter X-ray data. The material crystallizes in the triclinic space group $P\bar{1}$ with two dimeric formula units in a cell of dimensions $a = 11.463$ (12), $b = 9.893$ (11), $c = 22.757$ (25) Å; $\alpha = 90.06$ (2), $\beta = 93.04$ (2), $\gamma = 82.82$ (2)°. Least-squares refinement of 4453 independent data has led to an R factor of 0.074. The complex cation consists of two chromium(III) ions symmetrically bridged by two hydroxides, the remaining coordination sites being occupied by two bidentate 1,10-phenanthroline groups on each metal center. The coordination around each chromium center is roughly octahedral; the average Cr–N and Cr–O bond lengths are 2.056 (8) and 1.920 (3) Å, respectively, while the Cr–Cr separation is 2.986 (4) Å and the average Cr–O–Cr bridging angle is 102.1 (3)°. The magnetic susceptibility of a powdered sample of the complex has been examined in the temperature range 15–283°K. The dimer exhibits an antiferromagnetic exchange interaction, with the best fit to the Van Vleck equation including biquadratic exchange yielding $2J = -43.8$ cm^{-1} and $j = +1.5$ cm^{-1} with $\langle g \rangle = 2.00$. These data lead to a singlet–triplet splitting of -53.6 cm^{-1}. A comparison of the structural and magnetic properties of this complex with those of the glycinato complex $[Cr(gly)_2OH]_2$ leads to the conclusion that the correlation between bridging angle and singlet–triplet splitting observed for the analogous copper(II) complexes $[Cu(L)OH]_2^{2+}$ may also obtain for the chromium(III) systems.

Introduction

There has been considerable recent interest in the structural and magnetic properties of hydroxo-bridged copper(II) complexes of formulation $[Cu(L)OH]_2^{2+}$, where L is a bidentate ligand, and a number of structural and magnetic investigations on systems of this type have been reported.[1–13] These structural and magnetic data have demonstrated a nearly linear correlation between the Cu–O–Cu bridging angle, ϕ, and the singlet–triplet splitting, $2J$, with a slope of -79.1 cm^{-1} deg^{-1} and an intercept of 7730 cm^{-1}.[11] From molecular orbital considerations, it has been suggested that a similar relationship should exist for the analogous chromium(III) complexes $[Cr(L)_2OH]_2^{n+}$ but that the magnitude of the slope should be smaller for chromium(III) than for copper(II) because of the poor overlap between the chromium t_{2g} orbitals and the oxygen p orbitals relative to that between the copper $d_{x^2-y^2}$ orbital and the oxygen p orbitals.[12,14]

We have recently extended our experimental studies to the chromium complexes and have reported the structural and magnetic properties of the glycinato dimer,[15,16] $[Cr(gly)_2OH]_2$, and of the chloride salt of the phenanthroline dimer,[17] $[Cr(phen)_2OH]_2Cl_4 \cdot 6H_2O$. These latter data, which showed a singlet–triplet splitting of approximately -55 cm^{-1} for the chloride salt of the phen complex, are of considerable interest since, on the basis of high-temperature data, Earnshaw and Lewis[18] have calculated a singlet–triplet splitting of ap-

Table I. Positional and Thermal Parameters for the Nonring Atoms in $[Cr(phen)_2OH]_2I_4 \cdot 4H_2O$

Atom	x	y	z	β_{11}[a] (or B, Å^2)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I(1)	−0.07308 (8)	0.31621 (10)	0.39463 (4)	0.00844 (9)	0.01574 (13)	0.00228 (2)	−0.00230 (7)	0.00034 (3)	0.0004 (4)
I(2)	0.44148 (8)	0.30514 (9)	0.40443 (4)	0.00901 (9)	0.01442 (13)	0.00203 (2)	−0.00222 (7)	−0.00021 (3)	0.00136 (3)
I(3)	0.01452 (11)	0.25788 (15)	0.11273 (5)	0.01346 (12)	0.02668 (20)	0.00225 (3)	−0.00527 (11)	0.00033 (4)	−0.00037 (5)
I(4a)[b]	−0.5016 (5)	−0.18656 (13)	0.0757 (3)	0.0120 (5)	0.0421 (16)	0.0039 (1)	−0.0071 (7)	0.0002 (2)	0.0021 (3)
I(4b)[b]	−0.4712 (3)	−0.3110 (7)	0.0876 (2)	0.0158 (3)	0.0505 (10)	0.0056 (1)	−0.0115 (5)	0.0030 (1)	−0.0064 (3)
Cr(1)	−0.08687 (12)	−0.19938 (15)	0.24834 (7)	0.00423 (13)	0.00835 (18)	0.00116 (3)	−0.00154 (11)	0.00030 (5)	−0.00037 (6)
Cr(2)	0.17010 (13)	−0.29488 (15)	0.24402 (6)	0.00428 (13)	0.00781 (18)	0.00104 (3)	−0.00154 (10)	0.00034 (5)	0.00019 (5)
O(1)	0.0209 (6)	−0.3636 (7)	0.2457 (3)	0.0045 (5)	0.0080 (8)	0.0017 (2)	−0.0020 (5)	0.0006 (2)	−0.0009 (3)
O(2)	0.0623 (6)	−0.1303 (7)	0.2482 (3)	0.0048 (6)	0.0076 (8)	0.0018 (2)	−0.0016 (5)	0.0003 (2)	−0.0001 (3)
O(3)	−0.0655 (14)	0.4060 (15)	0.2464 (7)	8.2 (3)					
O(4)	0.1529 (12)	0.0920 (14)	0.2426 (6)	7.4 (3)					
O(5)	−0.2942 (12)	0.0854 (14)	0.4072 (6)	7.4 (3)					
O(6)	0.1957 (15)	0.1358 (16)	0.3556 (7)	8.7 (3)					

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Atom I(4a) was assigned 30% occupancy and atom I(4b) 70% occupancy.

proximately -14 cm^{-1} for the corresponding iodide salt. Hence, if the suggestion that there is a correlation between this parameter and the bridging geometry were correct, it appeared that the structure of the iodide salt must be considerably different from that of the chloride. Hence, we have undertaken a complete structural and magnetic investigation of the iodide salt of the 1,10-phenanthroline dimer, $[Cr(phen)_2OH]_2I_4 \cdot 4H_2O$.

Experimental Section

Suitable golden single crystals of the iodide salt were obtained by preparation of the nitrate salt by the method of Inskeep and Benson[19] and subsequent recrystallization from aqueous potassium iodide medium, and their identity was verified by chemical analysis.

After examination by precession and Weissenberg photography the crystals were assigned to the triclinic system; no systematic absences were observed, and the space group was assigned as either $P\bar{1}$ or $P1$. Successful refinement in the centrosymmetric space group $P\bar{1}$-C_i suggests that this is the correct assignment. The cell constants, obtained by least-squares methods[20] using 19 reflections, are a = 11.463 (12), b = 9.893 (11), c = 22.757 (25) Å; α = 90.06 (2), β = 93.04 (2), γ = 82.82 (2)°; these observations were made at 22° with the wavelength assumed as λ(Mo Kα_1) = 0.7093 Å. The density of 1.82 g cm^{-3} calculated for two dimeric units in the cell is in acceptable agreement with the value of 1.84 (2) g cm^{-3} observed by flotation in iodomethane–benzene solution. Hence, with two formula units in the cell, no crystallographic symmetry is imposed on the dimers.

Intensity data were collected from a parallelepiped-shaped crystal of dimensions 0.075 × 0.028 × 0.006 cm. The crystal was mounted along the long axis, which is roughly parallel to the crystallographic a axis. The crystal mosaicity was examined in the usual way[21] and was found to be acceptable. The data were collected in the manner described elsewhere[11] using a Picker four-circle automatic diffractometer equipped with a molybdenum tube and a graphite monochromator. The takeoff angle was 1.2°, the scan rate was 0.5 °/min, and the scan range was from 0.75° below the calculated Kα_1 peak position to 0.75° above the calculated Kα_2 peak position; backgrounds were counted for 40 sec at each end of the scan. A unique data set of 7924 reflections having 2θ(Mo) $\leq$ 48° was gathered, of which 5575 reflections had intensities greater than 3 times their estimated standard deviations.

The intensities of three standard reflections, measured after every 50 reflections, showed a continued decline so that, by the end of the run, the intensity of the average standard was only 97% of its original value; a linear correction for this decline in intensity with cumulative exposure was applied to the data.

The data were processed in the usual manner.[11,21] An absorption correction was applied; the linear absorption coefficient for this compound and Mo Kα radiation is 27.3 cm^{-1}, and for the sample chosen the transmission coefficients were in the range of 0.47–0.88.[22]

Solution and Refinement of the Structure

All attempts to solve the structure by the heavy-atom technique were unsuccessful, so the structure was solved by the direct-methods approach of Hauptman and Karle.[23] The locations of four iodine and two chromium atoms were obtained from an E map, and two cycles of least-squares refinement based on these positions gave values of the usual residuals $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ of 0.373 and 0.472, respectively. In all least-squares refinements in this analysis the function minimized was $\sum w(|F_o| - |F_c|)^2$, with the weights w being assigned as $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c, the atomic scattering factors for I and Cr were from Cromer and Waber,[24] those for O, N, and C were from Ibers,[25] and those for H were from Stewart, Davidson, and Simpson.[26] The effects of the anomalous dispersion of iodine and chromium were included in the calculation of F_c,[27] the values of $\Delta f'$ and $\Delta f''$ being taken from Cromer.[28]

In a subsequent difference Fourier map, the locations of all the remaining (except hydrogen) atoms were found. In addition to these peaks an extra large peak was observed close to one of the iodine positions which we took to be suggestive of possible disorder in this iodine position. A least-squares calculation including all of these atoms, with a 50:50 disorder applied to the apparently disordered iodine atom [I(4)], led to values of R_1 and R_2 of 0.146 and 0.224, respectively. Examination of the isotropic thermal parameters of the disordered position suggested that a 70:30 disorder was more appropriate, and a least-squares calculation based on this model gave R_1 = 0.133 and R_2 = 0.208. The assignment of variable anisotropic thermal parameters to the five iodine, two chromium, and the two bridging oxygen positions, with isotropic thermal parameters applied to the phenanthroline and water atoms, gave R_1 = 0.087 and R_2 = 0.136. The phenanthroline hydrogen atoms were included in calculated positions, assuming a C–H distance of 0.95 Å, in a least-squares calculation, giving R_1 = 0.083 and R_2 = 0.130.

Examination of a difference Fourier map demonstrated that our model for the disorder around I(4) was only approximate, since there remained several peaks in the range 1.0–1.3 e Å^{-3} in the vicinity of the two locations chosen; these peaks, however, could not be interpreted on the basis of any other useful disorder model. It appears probable that there is partial occupancy of more than two sites by I(4), but we have evidently chosen the two major sites. The presence of this large residual density in the difference Fourier map prevented us from locating the hydrogen atoms on the bridging oxygen atoms or on the water molecules. An examination of the agreement factor R_2 as a function of 2θ showed, as expected, that agreement for the low-order data was much worse than that for the higher order data; this phenomenon is presumably due to the effects of the residual density near I(4). Since we had a large number of data at our disposal, we elected to undertake a further refinement in which data with $2\theta \leq$ 25° were eliminated. This had the effect of reducing the number of data from 5575 to 4453 and reduced R_1 and R_2 to 0.074 and 0.092, respectively. The pronounced improvement in the value of R_2 was taken as evidence for the validity of our decision to eliminate the low-order data.

Since the low-order data had been eliminated, no correction for secondary extinction was applied. In the final cycle of least squares, no positional parameter exhibited a shift of more than 0.7 times its estimated standard deviation; this was taken as evidence that the refinement had converged. The final cycle involved, therefore, full-matrix refinement of 322 variables using 4453 independent intensities. The positional and thermal parameters for the nonring atoms are included in Table I and those for the phenanthroline carbon and nitrogen atoms in Table II. A table of observed and calculated

Table II. Positional and Thermal Parameters of the Phenanthroline Atoms

Atom	*x*	*y*	*z*	*B*, Å^2
AN1	−0.0851 (7)	−0.1782 (8)	0.3385 (4)	3.0 (1)
AC2	−0.0141 (10)	−0.1117 (11)	0.3723 (5)	3.4 (2)
AC3	−0.0196 (12)	−0.1116 (13)	0.4342 (6)	4.6 (2)
AC4	−0.0992 (15)	0.1813 (17)	0.4596 (7)	5.8 (3)
AC5	−0.2647 (14)	−0.3266 (15)	0.4478 (7)	5.3 (3)
AC6	−0.3394 (14)	−0.3853 (15)	0.4110 (7)	5.5 (3)
AC7	−0.4077 (13)	−0.4355 (14)	0.3057 (7)	4.9 (3)
AC8	−0.3984 (12)	−0.4172 (14)	0.2506 (6)	4.6 (2)
AC9	0.3077 (10)	−0.3486 (11)	0.2306 (5)	3.5 (2)
AN10	−0.2313 (7)	−0.2961 (8)	0.2666 (4)	3.0 (1)
AC11	−0.2446 (10)	−0.3114 (11)	0.3243 (5)	3.5 (2)
AC12	−0.1662 (9)	−0.2448 (10)	0.3636 (5)	3.0 (2)
AC13	−0.1728 (11)	−0.2480 (13)	0.4254 (6)	4.3 (2)
AC14	0.3305 (11)	0.3777 (12)	0.3490 (6)	4.0 (2)
BN1	−0.1859 (7)	−0.0118 (8)	0.2333 (4)	3.0 (1)
BC2	−0.2152 (11)	0.0839 (12)	0.2707 (5)	3.7 (2)
BC3	−0.2818 (13)	0.2072 (14)	0.2533 (6)	4.8 (3)
BC4	−0.3172 (13)	0.2304 (15)	0.1975 (7)	5.0 (3)
BC5	−0.3174 (14)	0.1371 (16)	0.0927 (7)	5.5 (3)
BC6	−0.2880 (16)	0.0420 (18)	0.0572 (8)	6.3 (3)
BC7	−0.1800 (17)	−0.1958 (19)	0.0399 (8)	6.4 (3)
BC8	−0.1208 (16)	−0.3088 (17)	0.0622 (8)	5.9 (3)
BC9	−0.0924 (11)	−0.3137 (13)	0.1232 (6)	4.4 (2)
BN10	0.1251 (8)	−0.2113 (9)	0.1594 (14)	3.7 (2)
BC11	−0.1854 (11)	−0.0980 (13)	0.1353 (6)	3.9 (2)
BC12	−0.2197 (10)	0.0096 (11)	0.1760 (5)	3.4 (2)
BC13	−0.2833 (12)	0.1254 (13)	0.1542 (6)	4.3 (2)
BC14	−0.2181 (14)	−0.0815 (15)	0.0776 (7)	5.2 (3)
CN1	0.1750 (8)	0.2697 (8)	0.1543 (4)	3.2 (2)
CC2	0.1359 (10)	−0.1613 (11)	0.1217 (5)	3.6 (2)
CC3	0.1370 (14)	−0.1610 (16)	0.0613 (7)	5.5 (3)
CC4	0.1810 (14)	−0.2748 (16)	0.0330 (7)	5.5 (3)
CC5	0.2854 (14)	0.4875 (16)	0.0411 (7)	5.6 (3)
CC6	0.3280 (14)	0.3843 (16)	0.0733 (7)	5.5 (3)
CC7	0.3707 (13)	0.2800 (15)	0.1743 (7)	5.2 (3)
CC8	0.3601 (12)	0.2985 (13)	0.2342 (6)	4.3 (2)
CC9	0.3063 (10)	0.4182 (12)	0.2557 (5)	3.5 (2)
CN10	0.2625 (7)	−0.4787 (8)	0.2218 (4)	3.1 (1)
CC11	0.2719 (9)	0.4949 (11)	0.1624 (5)	3.1 (2)
CC12	0.2223 (10)	−0.3803 (12)	0.1265 (5)	3.5 (2)
CC13	0.2285 (13)	−0.3892 (14)	0.0653 (7)	4.7 (3)
CC14	0.3250 (11)	0.3876 (13)	0.1370 (6)	4.0 (2)
DN1	0.3187 (7)	−0.1966 (8)	0.2600 (4)	2.8 (1)
DC2	0.3808 (9)	0.1379 (10)	0.2229 (5)	2.9 (2)
DC3	0.4743 (10)	−0.0658 (11)	0.2420 (5)	3.5 (2)
DC4	0.4996 (11)	−0.0513 (12)	0.3008 (6)	3.9 (2)
DC5	0.4584 (12)	−0.1087 (13)	0.4035 (6)	4.6 (2)
DC6	0.4002 (13)	−0.1766 (15)	0.4406 (7)	5.0 (3)
DC7	0.2482 (11)	−0.3366 (12)	0.4546 (6)	4.0 (2)
DC8	0.1651 (11)	−0.4084 (12)	0.4290 (6)	3.9 (2)
DC9	0.1421 (10)	−0.4037 (11)	0.3688 (5)	3.3 (2)
DN10	0.1998 (7)	−0.3291 (8)	0.3332 (4)	2.9 (1)
DC11	0.2837 (9)	−0.2584 (9)	0.3586 (4)	2.6 (2)
DC12	0.3473 (9)	−0.1867 (10)	0.3196 (5)	2.8 (2)
DC13	0.4364 (10)	−0.1138 (11)	0.3414 (5)	3.4 (2)
DC14	0.3120 (10)	−0.2583 (11)	0.4188 (5)	3.5 (2)

structure amplitudes is available.[29]

Description of the Structure

The structure consists of dimeric $[Cr(phen)_2OH]_2^{4+}$ cations which are well separated from the I^- anions but which may be involved in hydrogen bonding to two of the water molecules. The geometry of the cation is shown in Figure 1, and the inner coordination sphere around the chromium atoms is depicted in Figure 2.

The geometry around the chromium atoms is roughly octahedral, with two cis hydroxo groups and two cis phenanthroline ligands occupying the coordination sites. The bond lengths and angles in the cation are given in Table III. While the actual geometry of the dimer is C_1 (1), it approximates D_2 (222); hence, in this respect the geometry of this cation is different from that of the related dimers $[Cr(gly)_2OH]_2$ and $[Cr(ox)_2OH]_2^{4-}$ (where ox = oxalato), in which the geometry approximates C_{2h} (2/*m*).[14,16] The eight independent Cr–N distances are in the range 2.056 (10)–2.080 (8) Å, with an average distance of 2.066 (8) Å. This average separation is in excellent agreement with the values of 2.061 (5) and 2.066 (5) Å found[16] in $[Cr(gly)_2OH]_2$, 2.068 (1) Å in[30] $[Cr(gly)_3]\cdot H_2O$, 2.075 (2) and 2.081 (5) Å in[31,32] $Cr(en)_3^{3+}$ (en = ethylenediamine), and the value of 2.052 (6) Å found[17] in the chloride salt of this cation; the absence of any detectable shortening of the Cr–N separation here suggests that there is little multiple bonding between the metal and the aromatic phenanthroline ligands.

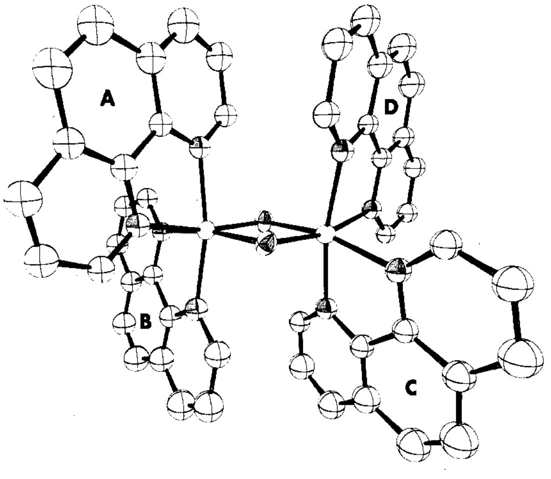


Figure 1. View of the $[Cr(phen)_2OH]_2^{4+}$ cation in $[Cr(phen)_2OH]_2I_4\cdot 4H_2O$. A, B, etc. correspond to phen A, phen B, etc. in the text. Hydrogen atoms are omitted for clarity.

Table III. Selected Intramolecular Distances and Angles in $[Cr(phen)_2OH]_2I_4\cdot 4H_2O$

Intramolecular Distances, Å

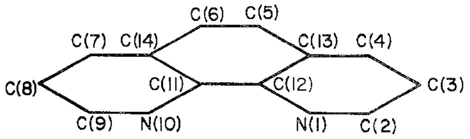
Cr(1)–Cr(2)	2.986 (4)	Cr(1)–BN(1)	2.070 (9)
Cr(1)–O(1)	1.917 (7)	Cr(1)–BN(10)	2.056 (10)
Cr(1)–O(2)	1.919 (7)	Cr(2)–CN(1)	2.062 (9)
Cr(2)–O(1)	1.920 (7)	Cr(2)–CN(10)	2.064 (9)
Cr(2)–O(2)	1.923 (7)	Cr(2)–DN(1)	2.080 (8)
Cr(1)–AN(1)	2.061 (9)	Cr(2)–DN(10)	2.061 (9)
Cr(1)–AN(10)	2.073 (9)		

Intramolecular Angles, Deg

O(1)–Cr(1)–O(2)	78.0 (3)	Cr(1)–O(1)–Cr(2)	102.2 (3)
O(1)–Cr(2)–O(2)	77.8 (3)	Cr(1)–O(2)–Cr(2)	102.0 (3)
AN(1)–Cr(1)–AN(10)	79.9 (3)	CN(1)–Cr(2)–CN(10)	79.5 (3)
AN(1)–Cr(1)–O(1)	97.9 (3)	CN(1)–Cr(2)–O(1)	98.5 (3)
AN(1)–Cr(1)–O(2)	89.6 (3)	CN(1)–Cr(2)–O(2)	90.2 (3)
AN(1)–Cr(1)–BN(1)	93.2 (3)	CN(1)–Cr(2)–DN(1)	92.1 (3)
AN(1)–Cr(1)–BN(10)	168.3 (4)	CN(1)–Cr(2)–DN(10)	169.0 (3)
AN(10)–Cr(1)–O(1)	95.2 (3)	CN(10)–Cr(2)–O(1)	95.0 (3)
AN(10)–Cr(1)–O(2)	166.6 (3)	CN(10)–Cr(2)–O(2)	166.5 (3)
AN(10)–Cr(1)–BN(1)	93.9 (3)	CN(10)–Cr(2)–DN(1)	95.1 (3)
AN(10)–Cr(1)–BN(10)	91.3 (4)	CN(10)–Cr(2)–DN(10)	93.7 (3)
BN(1)–Cr(1)–O(1)	166.8 (3)	DN(1)–Cr(2)–O(1)	166.5 (3)
BN(1)–Cr(1)–O(2)	94.9 (3)	DN(1)–Cr(2)–O(2)	93.9 (3)
BN(1)–Cr(1)–BN(10)	79.7 (4)	DN(10)–Cr(2)–DN(10)	79.7 (3)
BN(10)–Cr(1)–O(1)	90.4 (3)	DN(10)–Cr(2)–O(1)	90.7 (3)
BN(10)–Cr(1)–O(2)	100.2 (3)	DN(10)–Cr(2)–O(2)	97.7 (3)

The Cr–O distances in the bridging unit are in the range 1.917 (7)–to 1.923 (7) Å, with an average value of 1.920 (3) Å. These values are again similar to those found[17] in the chloride salt and are shorter than those in[16] $[Cr(gly)_2OH]_2$ but are similar to values found for Cu–O bridges in a variety of copper(II) complexes.[1-3,7-9,11] The Cr–O–Cr–O bridging unit is planar, with all atoms falling within 0.009 Å of the best unweighted least-squares plane, but the "in-plane" nitrogen atoms lie from 0.37 to 0.44 Å from this plane. The Cr(1)–Cr(2) separation of 2.986 (4) Å is longer than the value of 2.974 (2) Å in $[Cr(gly)_2OH]_2$ and slightly shorter than that of 3.008 (3) Å found in the chloride salt. There is, however, a great difference between the bridging angles of the phen and

Table IV. Intramolecular Distances (Å) in the Phenanthroline Ligands of $[Cr(phen)_2OH]_2^{4+}$



Atoms	Phen A	Phen B	Phen C	Phen D	Average	π order
N(1)-N(10)	2.653 (9)	2.644 (10)	2.639 (10)	2.654 (9)	2.648 (7)	
N(1)-C(2)	1.323 (15)	1.296 (16)	1.321 (16)	1.315 (14)	1.314 (12)	0.6
C(2)-C(3)	1.415 (20)	1.401 (21)	1.376 (22)	1.410 (17)	1.401 (17)	0.4
C(3)-C(4)	1.362 (24)	1.325 (23)	1.353 (25)	1.365 (19)	1.351 (18)	0.6
C(4)-C(13)	1.350 (24)	1.462 (22)	1.387 (24)	1.396 (18)	1.399 (47)	0.4
C(13)-C(5)	1.495 (23)	1.434 (24)	1.434 (24)	1.424 (20)	1.447 (33)	0.2
C(5)-C(6)	1.361 (25)	1.264 (25)	1.287 (24)	1.336 (22)	1.312 (44)	0.8
C(6)-C(14)	1.402 (23)	1.438 (26)	1.453 (23)	1.439 (21)	1.433 (22)	0.2
C(14)-C(7)	1.454 (21)	1.455 (27)	1.394 (22)	1.415 (19)	1.430 (30)	0.4
C(7)-C(8)	1.278 (22)	1.321 (28)	1.385 (23)	1.365 (20)	1.337 (48)	0.6
C(8)-C(9)	1.406 (20)	1.408 (25)	1.368 (20)	1.381 (19)	1.391 (20)	0.4
C(9)-N(10)	1.320 (16)	1.334 (18)	1.312 (15)	1.348 (15)	1.329 (16)	0.6
N(10)-C(11)	1.341 (16)	1.343 (17)	1.368 (15)	1.363 (14)	1.354 (14)	0.4
C(11)-C(12)	1.451 (17)	1.441 (19)	1.439 (18)	1.422 (15)	1.438 (12)	0.2
C(12)-N(1)	1.355 (15)	1.352 (16)	1.333 (16)	1.385 (15)	1.356 (22)	0.4
C(12)-C(13)	1.413 (19)	1.359 (19)	1.399 (21)	1.392 (17)	1.391 (23)	0.4
C(11)-C(14)	1.391 (18)	1.351 (22)	1.385 (19)	1.393 (17)	1.380 (20)	0.4

Table V. Internal Bond Angles (deg) in the Phenanthroline Ligands in $[Cr(phen)_2OH]_2^{4+}$

Atoms	Phen A	Phen B	Phen C	Phen D	Av
C(2)-N(1)-C(12)	119.4 (9)	118.6 (9)	117.3 (10)	118.2 (8)	118.4 (9)
N(1)-C(2)-C(3)	121.2 (10)	121.9 (11)	122.9 (11)	122.0 (10)	122.0 (7)
C(2)-C(3)-C(4)	119.5 (13)	120.8 (13)	119.8 (14)	119.8 (11)	120.0 (6)
C(3)-C(4)-C(13)	119.7 (15)	118.5 (13)	119.5 (15)	119.6 (11)	119.3 (6)
C(6)-C(5)-C(13)	121.1 (14)	121.5 (15)	122.4 (15)	121.9 (12)	121.8 (5)
C(5)-C(6)-C(14)	121.2 (14)	120.6 (16)	121.8 (14)	120.6 (13)	121.1 (6)
C(8)-C(7)-C(14)	120.9 (13)	120.8 (17)	117.7 (13)	119.4 (11)	119.7 (15)
C(7)-C(8)-C(9)	120.4 (13)	118.1 (16)	120.9 (12)	120.4 (11)	120.0 (13)
C(8)-C(9)-N(10)	122.9 (11)	123.1 (12)	122.9 (11)	122.1 (10)	122.8 (4)
C(9)-N(10)-C(11)	116.1 (9)	117.4 (10)	117.2 (9)	117.7 (9)	117.1 (7)
N(10)-C(11)-C(14)	125.8 (11)	124.9 (12)	123.6 (10)	123.7 (9)	124.5 (10)
C(12)-C(11)-C(14)	118.0 (10)	119.6 (12)	120.6 (11)	120.0 (9)	119.6 (11)
N(1)-C(12)-C(13)	120.7 (10)	124.5 (11)	123.9 (11)	122.6 (9)	122.9 (17)
C(11)-C(12)-C(13)	122.3 (10)	118.0 (11)	119.0 (11)	120.3 (10)	119.9 (19)
C(4)-C(13)-C(12)	119.5 (12)	115.7 (12)	116.5 (13)	117.6 (10)	117.3 (16)
C(5)-C(13)-C(12)	124.9 (13)	120.3 (12)	118.3 (13)	118.4 (10)	120.5 (31)
C(6)-C(14)-C(11)	121.7 (12)	120.0 (14)	117.7 (12)	118.5 (11)	119.5 (18)
C(7)-C(14)-C(11)	113.7 (11)	115.7 (14)	117.7 (12)	116.8 (10)	115.0 (17)

gly complexes; the values of 102.0 (3) and 102.2 (3)° here are much greater than that of 98.2 (2)° in $[Cr(gly)_2OH]_2$ and slightly smaller than the average value of 102.7 (5)° in the chloride salt. Each of the bridging hydroxides may be involved in a hydrogen bond with a neighboring water molecule, with O(1)····O(3) and O(2)····O(4) distances of 2.60 (2) and 2.55 (1) Å, respectively. Our inability to locate the hydrogen atoms on O(1) and O(2) renders us unable to calculate the O–H···O angles, but these separations are considerably shorter than twice the value of 1.40 Å given by Pauling[33] for the van der Waals radius of oxygen.

The bond distances and angles found in the four independent 1,10-phenanthroline ligands are listed in Tables IV and V. Also shown in Table IV is the fraction of π character associated with each bond in the parent hydrocarbon phenanthrene as calculated by valence-bond techniques.[33] As was also seen in a variety of other phenanthroline complexes,[17,34-36] the average C–N and C–C bond lengths correlate well with these calculated π-bond orders. Thus, while the precision of these distances is limited, it appears that the longest C–C bonds are C(5)–C(13), C(6)–C(14), and C(11)–C(12), which have 20% double-bond character, and the shortest is C(5)–C(6), which has 80% double-bond character. The average N···N bite of 2.648 (7) Å is again similar to the values 2.62–2.72 Å found in other phenanthroline complexes.[17,34-36]

The phenanthroline ligands, as can be seen from an examination of Table VI, deviate markedly from planarity, but we are not able to discern any physically meaningful trend. This nonplanarity of the phenanthroline groups, which renders group refinement[37] impossible, has been observed by many other workers[17,34,38-41] and must be considered real. The chromium atoms do not lie exactly in the best unweighted least-squares planes through the phenanthrolines; thus, Cr(1) is 0.22 and 0.05 Å out of the planes through phen A and phen B, respectively, and Cr(2) is 0.16 and 0.32 Å out of the planes through phen C and phen D, respectively.

Table VI. Distances (Å) of the Phenanthroline Atoms from Their Respective Least-Squares Planes

Atom	Phen A	Phen B	Phen C	Phen D
N(1)	−0.050	0.005	0.021	−0.053
C(2)	0.017	0.005	−0.044	0.025
C(3)	0.067	−0.007	−0.035	0.098
C(4)	0.043	−0.016	0.025	0.040
C(5)	−0.023	−0.012	−0.008	−0.044
C(6)	−0.008	−0.015	−0.004	−0.028
C(7)	0.016	0.020	−0.021	0.064
C(8)	0.084	−0.017	−0.015	0.073
C(9)	0.030	−0.015	0.006	0.012
N(10)	−0.043	−0.013	0.016	−0.060
C(11)	−0.062	0.021	0.011	−0.054
C(12)	−0.040	0.012	0.031	−0.057
C(13)	−0.008	0.015	0.028	−0.025
C(14)	−0.021	0.017	−0.011	0.009

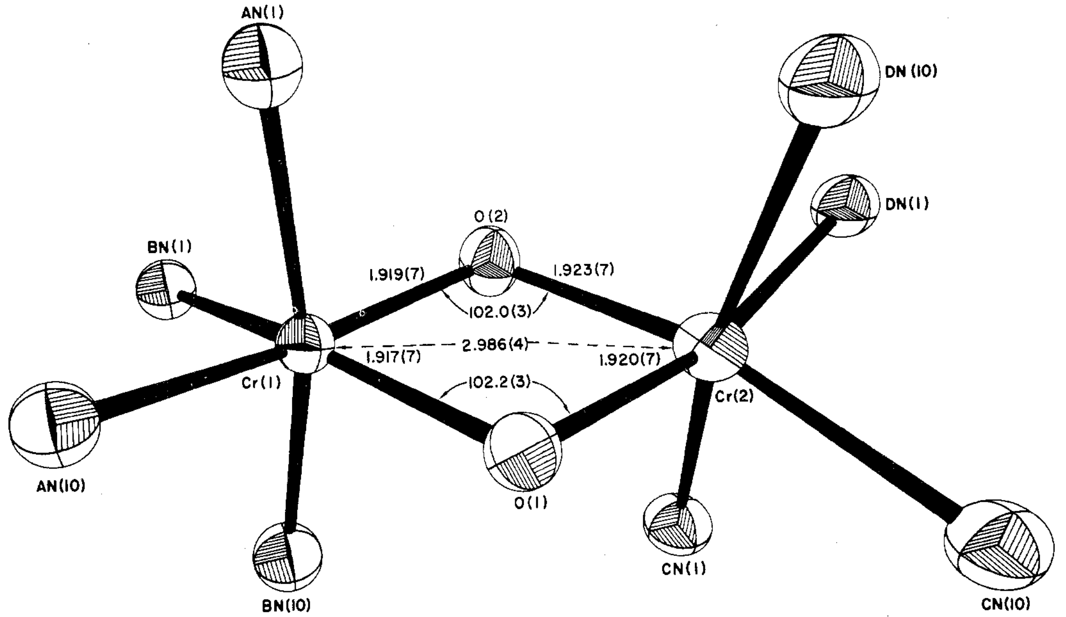


Figure 2. The coordination around the chromium centers in $[Cr(phen)_2OH]_2I_4 \cdot 4H_2O$. Atom AN1 is nitrogen 1 of group phen A, etc.

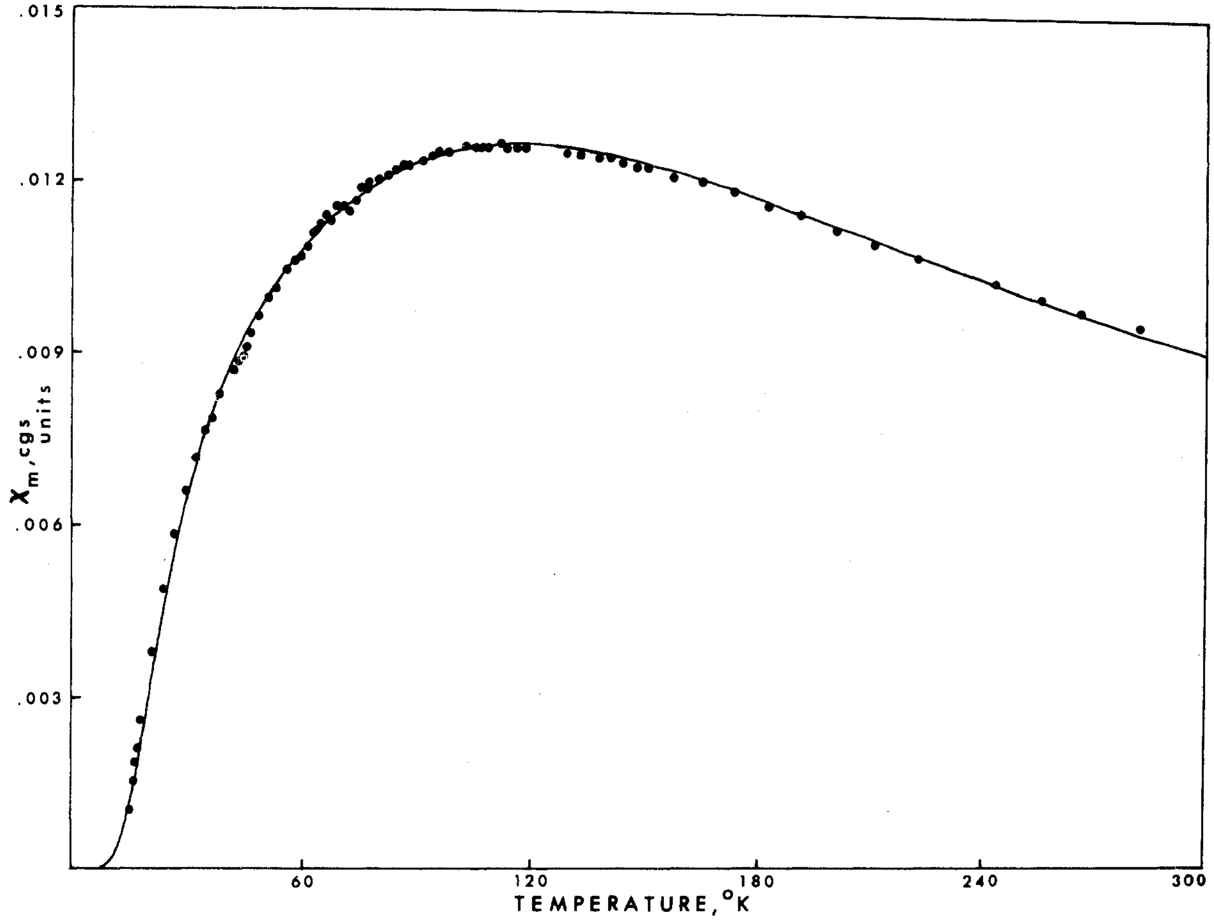


Figure 3. The temperature dependence of the magnetic susceptibility of $[Cr(phen)_2OH]_2I_4 \cdot 4H_2O$. The experimental data are shown as dots and the best fit to the dimer ($S = {}^3/_2, {}^3/_2$) equation including biquadratic exchange is displayed as the full line.

The three iodide ions which do not show disorder are apparently involved in hydrogen bonding with the water molecules, while the disordered iodide positions are both more than 4 Å from all water oxygen atoms. The sum of the van der Waals radius of oxygen and the ionic radius of iodide ion is given as 3.56 Å by Pauling[33] and 3.68 Å by Bondi.[42] I(1) is located at distances of 3.50 (2), 3.52 (2), and 3.64 (1) Å from water oxygen atoms O(3), O(5), and O(6), respectively, I(2) is 3.50 (1) and 3.58 (2) Å from O(5) and O(6), respectively, and I(3) is 3.49 (2) and 3.58 (1) Å from O(3) and O(4), respectively. Hamilton and Ibers have suggested[43] that the criterion for hydrogen bonding is that both the O–H and H···I separations are less than their respective radius sums, but our inability to locate the hydrogen atoms on the water molecules prevents us from using this concept. It is probable, however, that all of the separations listed above are the result of some hydrogen-bonding interactions between the anions and the solvent molecules. It is noteworthy that atom I(1), which appears to be involved in the most hydrogen bonds, exhibits the least thermal motion.

Magnetic Properties

The magnetic susceptibility of a powdered sample of the chromium dimer was measured from 15 to 283°K using a Foner-type PAR vibrating-sample magnetometer.[44] All susceptibility measurements were obtained at a field strength of 10,000 G. Temperatures were measured by a calibrated gallium arsenide diode, and mercury tetrathiocyanatocobaltate(II) was used as the susceptibility standard.[45]

The experimental results display a broad maximum value of the susceptibility at about 113°K, indicative of antiferromagnetic superexchange coupling. The experimental data did not satisfactorily conform to theoretical values obtained according to[46]

$$\chi_{\mathrm{m}} = \frac{Ng^2\beta^2}{kT} \times \left[\frac{2\exp(2J/kT) + 10\exp(6J/kT) + 28\exp(12J/kT)}{1 + 3\exp(2J/kT) + 5\exp(6J/kT) + 7\exp(12J/kT)}\right] \quad (1)$$

where J is the exchange coupling constant of two atoms of a dimer each with $S = {}^3/_2$ and where χ_{m} is the theoretical calculated molar susceptibility of the dimer.

The thermomagnetic behavior of certain other chromium(III) dimers[16,47] has been satisfactorily explained by including biquadratic exchange interactions in the general-exchange Hamiltonian[48]

$$H_{\mathrm{c}} = -2J(S_1 \cdot S_2) - j(S_1 \cdot S_2)^2 \quad (2)$$

where j is the biquadratic exchange constant. Use of the biquadratic term in the Hamiltonian results in the following expanded expression for χ_{m}

$$\chi_{\mathrm{m}} = \frac{Ng^2\beta^2}{kT} \times \left[\frac{2\exp[(2J - 6.5j)/kT] + 10\exp[(6J - 13.5j)/kT] + 28\exp[(12J - 9j)/kT]}{1.0 + 3\exp[(2J - 6.5j)/kT] + 5\exp[(6J - 13.5j)/kT] + 7\exp[(12J - 9j)/kT]}\right] \quad (3)$$

The linear least-squares fit of the experimental data to theoretical susceptibilities generated by eq 3, as shown in Figure 3, provides excellent agreement between experimental results and theory when $2J = -43.8$ cm^{-1} and $j = +1.5$ cm^{-1}, with $\langle g \rangle = 2.00$. We therefore conclude that the $[\mathrm{Cr(phen)_2OH}]_2\mathrm{I_4 \cdot 4H_2O}$ dimer exhibits an antiferromagnetic exchange interaction with the difference in energy between the $S' = 0$ ground state and $S' = 1$ excited state being equal to 53.6 cm^{-1}. Second-order exchange interactions appear to be necessary to describe the magnetic behavior of the compound.

Hence, since the singlet–triplet splitting, ΔE, observed in the present case is −53.6 cm^{-1} while that in $[\mathrm{Cr(gly)_2OH}]_2$ is −10.0 cm^{-1} [49] and the bridging angle ϕ is 102.1 (3)° while that in $[\mathrm{Cr(gly)_2OH}]_2$ is 98.2 (2)°, we apparently do observe a trend in ΔE *vs.* ϕ which is similar to that found in the analogous copper(II) systems (*vide supra*). Moreover, as anticipated, the magnitude of the antiferromagnetic interaction in the chromium systems is evidently smaller than that in the copper complexes, since for $[\mathrm{Cu(teen)OH}]_2^{2+}$ (teen = *N*,*N*,*N'*,*N'*-tetraethylethylenediamine) $\Delta E = -410$ cm^{-1} and $\phi = 103.0°$,[11] while in $[\mathrm{Cr(phen)_2OH}]_2^{4+}$ $\phi = 102.1°$ and ΔE is only −54 cm^{-1}. In order to further our investigations of chromium(III) dimers of this type, we are extending our structural and magnetic investigations to other similar systems.

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Registry No. $[\mathrm{Cr(phen)_2OH}]_2\mathrm{I_4 \cdot 4H_2O}$, 54162-92-4.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC40599Q.

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The Phenyldiazo Group as a Bridging Ligand. Crystal Structure and Molecular Configuration of Bis(tetracarbonylphenyldiazomanganese), $[PhN{=}NMn(CO)_4]_2$, Including the Location and Refinement of the Hydrogen Atoms

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Bis(tetracarbonylphenyldiazomanganese), $[PhN{=}NMn(CO)_4]_2$, crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ [C_i^1; No. 2] with $a = 7.236$ (1) Å, $b = 8.889$ (2) Å, $c = 9.468$ (2) Å, $\alpha = 80.52$ (2)°, $\beta = 77.38$ (1)°, $\gamma = 71.44$ (1)°, and $V = 560.4$ Å^3. The observed density is 1.59 (2) g cm^{-3}, while ρ(calcd) = 1.613 g cm^{-3} for mol wt 544.2 and $Z = 1$. Single-crystal X-ray diffraction data complete to $2\theta = 50°$ (Mo Kα radiation) were collected with a Picker FACS-1 diffractometer and the structure was solved using conventional Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogens, were located, the final discrepancy indices being $R_F = 3.43\%$ and $R_{wF} = 3.61\%$ for the 1974 independent reflections (none rejected). The $[PhN{=}NMn(CO)_4]_2$ molecule lies on a crystallographic center of symmetry. The two manganese atoms are separated by 3.235 (1) Å and are bridged by two μ-phenyldiazo ligands. The bridges are not, however, symmetrical; thus Mn–N(1) = 2.031 (2) Å *vs.* Mn'–N(1) = 2.023 (2) Å and Mn–N(1)–N(2) = 134.5 (1)° as opposed to Mn'–N(1)–N(2) = 119.5 (1)°.

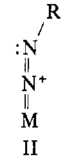
Introduction

Transition metal complexes having aryldiazo (R—N═N–, R = aryl) ligands in terminal positions have been known for some time.[1-6] The study of such complexes has been given considerable impetus as a result of (i) the suggestion that these systems may be used as models for the enzymatic reduction of dinitrogen[2] and (ii) the fact that the aryldiazo system is isoelectronic with nitric oxide in its bonding to transition metal atoms.

As with nitric oxide, the aryldiazo ligand may coordinate to a transition metal in either a linear or a bent manner; within the framework of the valence-bond approach, the aryldiazo ligand can be regarded as behaving as RN_2^+ (when the M–N–N system is linear) and as RN_2^- (when the M–N–N system is bent, with an angle of *ca.* 120°). Each of these cases has, in fact, been observed. Thus, the complexes $(PPhMe_2)_3Re(N{=}NPh)Cl_2$,[7] $(HB(pz)_3)Mo(CO)_2(N{=}NPh)$,[8] and $(PPh_3)_2Ru(N{=}N(p\text{-tol}))Cl_3$[9] each have rather short metal–nitrogen bond lengths (Re–N = 1.80 (1) Å,[7] Mo–N = 1.825 (4) Å,[8] and Ru–N = 1.796 (9) Å[9]) and have essentially linear M–N–N structural units (Re–N–N = 172°,[7] Mo–N–N = 174.21 (12)°,[8] and Ru–N–N = 171.2 (9)°[9]). Such a stereochemical arrangement is consistent with the aryldiazo ligand being considered as RN_2^+ and may be represented by forms I and II. Form II would seem to be preferred, for the N-N-R angles are 118° in $(PPhMe_2)_3Re(N{=}NPh)Cl_2$,[7] 121.09 (21)° in $(HB(pz)_3)Mo(CO)_2(N{=}NPh)$,[8] and 135.9 (11)° in $(PPh_3)_2Ru(N{=}N(p\text{-tol}))Cl_3$.[9] [pz = pyrazolyl.]

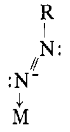

$R-\overset{+}{N}\equiv N\rightarrow{:}M$

I


$R-\ddot{N}{=}\overset{+}{N}{=}M$

II

In contrast to this, a structural study of the $[\{PhP((CH_2)_3PPh_2)_2\}Rh(N{=}NPh)Cl]^+$ ion[10] has revealed "doubly bent" coordination of a phenyldiazo ligand to rhodium (Rh–N–N = 125 (1)° and N–N–Ph = 119 (1)°) along with a normal rhodium–nitrogen distance of 1.954 (8) Å. This geometric pattern is consistent with the aryldiazo ligand behaving formally as RN_2^-; the valence-bond description of the aryldiazometal moiety in this system is shown as III.


$R-\ddot{N}{=}\overset{-}{N}{:}\rightarrow M$

III

Recently, Abel and coworkers[11] have shown that (trimethylsilyl)phenyldiimine ($Me_3SiN{=}NPh$) reacts with bromopentacarbonylmanganese, with loss of Me_3SiBr and CO, yielding $[PhN{=}NMn(CO)_4]_2$, a unique complex with *bridging* phenyldiazo groups. In order to obtain detailed stereochemical information on this newly discovered mode of bonding for an aryldiazo ligand, we have subjected this complex to a full three-dimensional single-crystal X-ray structural analysis. A preliminary account of this work has appeared previously;[12] a full description is reported below.

Collection of the X-Ray Diffraction Data

Transparent yellow crystalline plates of $[PhN{=}NMn(CO)_4]_2$ were provided by Professor E. W. Abel of the University of Exeter, Exeter, England. The crystal used during the structural analysis was a thin platelike parallelepiped with six faces, dimensions being $(001)\rightarrow(00\bar{1}) = 0.072$ mm, $(010)\rightarrow(0\bar{1}0) = 0.550$ mm, and $(110)\rightarrow(\bar{1}\bar{1}0) = 0.724$ mm. The crystal was mounted along [211]. Preliminary photographs of the reciprocal lattice showed no systematic absences and revealed no symmetry other than C_i ($\bar{1}$) Friedel symmetry. The crystal was therefore assumed to belong to the triclinic system, possible space groups being the noncentrosymmetric $P1$ [C_1^1; No. 1] and the centrosymmetric $P\bar{1}$ [C_i^1; No. 2].[13]

The crystal was transferred to a Picker FACS-1 diffractometer, was accurately centered, and was aligned precisely along [211]. The intensity of the axial 422 reflection was measured by a θ–2θ scan at $\chi = 90°$ and at 10° intervals from $\phi = 0°$ to $\phi = 350°$. The observed variation in intensity [(maximum – minimum)/(average) = 18.3%] indicated that an absorption correction would be necessary.

Details of the data collection are given in Table I; a description