

X-ray Structural Characterization of the Congeneric Complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})_2\text{Cl}]$ ($M = \text{Cr}$ or W)

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Abstract

The structures of the complexes chloro(η^5 -cyclopentadienyl)dinitrosylchromium and -tungsten have been redetermined and determined, respectively, by three-dimensional, single-crystal X-ray diffraction methods. Crystal data are as follows: $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2\text{Cl}]$: orthorhombic, space group $P2_12_12_1$, $a = 10.8016$ (9), $b = 12.2586$ (13), $c = 5.9564$ (6) Å, $V = 788.70$ (2) Å³, $Z = 4$. $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{Cl}]$: triclinic, space group $P\bar{1}$, $a = 9.8642$ (9), $b = 6.8478$ (9), $c = 6.8510$ (6) Å, $\alpha = 69.700$ (9), $\beta = 73.135$ (7), $\gamma = 88.228$ (9)°, $V = 414.10$ (2) Å³, $Z = 2$. Diffraction data for each complex were collected with an Enraf–Nonius CAD-4 diffractometer (Mo $K\alpha$ radiation); the structures were refined by conventional full-matrix, least-squares techniques. Final discrepancy indices were $R = 0.023$ and $R_w = 0.032$ for the Cr complex (957 observed reflections) and $R = 0.026$ and $R_w = 0.029$ for the W complex (2147 observed reflections). In terms of their gross stereochemical features, the two molecules are isostructural, having ‘piano-stool’ configurations. The principal structural difference occurs in the $M\text{—Cl}$ bond distances, the Cr–Cl and W–Cl distances being 2.321 (1) and 2.386 (3) Å, respectively. The relatively long Cr–Cl distance suggests somewhat greater ionic character for this linkage, an interpretation which is in accord with the observed physical and chemical properties of both complexes.

Introduction

During our previous work with Group 6B organometallic nitrosyl complexes, we observed that the compounds $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})_2\text{Cl}]$ ($M = \text{Cr}, \text{Mo}$ or W) exhibit several interesting trends in their physical (Legzdins & Malito, 1975; Botto, Kolthammer, Legzdins & Roberts, 1979) and chemical (Hoyano, Legzdins & Malito, 1975; Legzdins & Martin, 1979) properties as the atomic weight of M increases. With a view toward rationalizing these trends, we undertook an X-ray crystallographic investigation of the first and last members of this series. In this paper we report the results of this study.

Experimental

The complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2\text{Cl}]$ (I) and $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{Cl}]$ (II) were prepared according to published procedures (Hoyano, Legzdins & Malito, 1978). Single crystals of both compounds suitable for crystallographic study were obtained by slow cooling of dichloromethane–hexane solutions from 313 K to room temperature. Crystals of both (I) and (II) were selected

Table 1. *Crystal data and Enraf–Nonius CAD-4 data-collection procedures for $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2\text{Cl}]$ (I) and $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{Cl}]$ (II)*

	(I)	(II)
Formula	$\text{C}_5\text{H}_5\text{ClCrN}_2\text{O}_2$	$\text{C}_5\text{H}_5\text{ClW}_2\text{O}_2$
M_r	212.6	344.4
Space group	$P2_12_12_1$	$P\bar{1}$
a (Å)	10.8016 (9)	9.8642 (9)
b (Å)	12.2586 (13)	6.8478 (9)
c (Å)	5.9564 (6)	6.8510 (6)
α (°)		69.700 (9)
β (°)		73.135 (7)
γ (°)		88.228 (9)
V (Å ³)	788.70 (2)	414.10 (2)
Z	4	2
ρ_c (Mg m ⁻³)	1.790	2.761
ρ_m (Mg m ⁻³)	—	2.75 (2)
Radiation	Graphite-monochromated Mo $K\alpha$	
Crystal bounding planes	{100}, {001}, {110}	{100}, {001}, {111}, {110} and inverses
Crystal volume (mm ³)	0.0184	0.0172
μ (Mo $K\alpha$) (mm ⁻¹)	1.64	13.63
Transmission factors (I)	0.582–0.854	0.063–0.131
Monochromator angle (°)	12.20 (2 θ)	12.20 (2 θ)
Scan type	ω -2 θ	ω -2 θ
Scan width ($\Delta\omega$) (°)	0.60 + 0.35 tan θ	0.65 + 0.35 tan θ
Aperture width (mm)	1.5 + tan θ	1.5 + tan θ
Crystal-counter distance (mm)	173	173
Prescan rejection limit	0.5 (2 σ)	0.667 (1.5 σ)
Prescan acceptance limit	0.033 (30 σ)	0.033 (30 σ)
Maximum scan speed (° min ⁻¹)	10.06	10.06
Maximum counting time (s)	60	50
Collection range	$+h, +k, +l$ $1^\circ < \theta \leq 27.5^\circ$	$h, \pm k, \pm l$ $1^\circ < \theta \leq 30^\circ$
Unique data	1064	2387
Unique data with $I > 3\sigma(I)$	957	2147
p	0.05	0.05
X-ray exposure time (h)	10	22
Crystal decomposition	Negligible	Negligible

via a series of precession photographs which also provided initial unit-cell parameters, the Laue symmetry, and the space groups $P2_12_12_1$ for (I) and $P1$ or $P\bar{1}$ for (II). A least-squares analysis of the setting angles of 25 reflections [$16^\circ < \theta < 21^\circ$ for (I); $20^\circ < \theta < 25^\circ$ for (II)], automatically located and centered on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated $\text{Mo } K\alpha$ radiation, provided accurate unit-cell parameters (Table 1). Data were collected at room temperature using the CAD-4 parameters and the procedures summarized in Table 1. Both data sets were corrected for Lorentz and polarization effects, and a Gaussian integration absorption correction (Busing & Levy, 1957; Coppens, Leiserowitz & Rabinovich, 1965) was applied.

The published atomic parameters for (I) (Carter, McPhail & Sim, 1966) were refined by full-matrix least squares including anomalous-dispersion components for Cr and Cl (Cromer & Liberman, 1970), an isotropic extinction parameter g (Becker & Coppens, 1974, 1975), and weights $1/\sigma^2(F)$. Scattering factors were taken from Cromer & Mann (1968). The resulting R value for the 957 observed, absorption-corrected intensities was 0.041 with Cr, Cl, N, and O anisotropic and (1:1) disordered isotropic C atoms in the $(\eta^5\text{-C}_5\text{H}_5)_2$ ligand. Inversion of the structure to $-x, y, z$ followed by two further cycles of least-squares refinement reduced R to 0.037 with $R_w = 0.055$ (versus 0.061 for the

initial refinement), thereby clearly indicating the chirality of the chosen crystal. The C atom thermal parameters suggested that a weight of 0.5 was acceptable, even though the cyclopentadienyl ring geometries were somewhat uneven. By allowing the C atoms to refine anisotropically, the ring geometries were much improved, R was reduced to 0.027, and a difference Fourier synthesis contained peaks at the expected positions of the H atoms. Idealized positions for these half-weight H atoms were calculated ($\text{C-H} = 0.95 \text{ \AA}$, X-ray determination), and they were included in the model with isotropic B values set at 110% of the converged isotropic equivalent of the C atom to which they were bonded. The H atom scattering factors were taken from Stewart, Davidson & Simpson (1965). Further least-squares refinement with fixed H atom parameters reduced R to the final value of 0.023, with $R_w = 0.032$ for the 957 observed reflections. Shift/error ratios of up to 2.5 for the disordered C parameters, related by correlation coefficients as high as 0.9, could not be improved by repeated cycles of least squares. The average shift/error for the full-weight atoms was 0.09 in the last cycle. The final value of g was $3.8(4) \times 10^4$ and the function minimized was $\sum w(|F_o| - |F_c|)^2$; weighting analyses confirmed the suitability of the chosen $1/\sigma^2(F)$ weights. A final difference Fourier synthesis contained peaks of up to $\pm 0.3 \text{ e \AA}^{-3}$ in the region of the heavy atoms and up to $\pm 0.2 \text{ e \AA}^{-3}$ elsewhere. Final atomic positional parameters are presented in Table 2.*

Table 2. Final positional parameters for $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}(\text{NO})_2\text{Cl}]$ (fractional $\times 10^3$; for Cr and Cl $\times 10^5$; for N and O $\times 10^4$) with estimated standard deviations in parentheses

	x	y	z
Cr	2727 (4)	64191 (3)	43203 (7)
Cl	-2369 (10)	78982 (7)	65705 (16)
N(1)	1433 (3)	5863 (2)	5924 (5)
O(1)	2209 (4)	5364 (3)	6782 (7)
N(2)	1277 (2)	7019 (3)	2459 (5)
O(2)	1914 (3)	7278 (3)	987 (5)
Cp(11)	-106 (4)	611 (4)	150 (4)
Cp(12)	-175 (2)	642 (1)	333 (3)
Cp(13)	-155 (2)	565 (2)	498 (3)
Cp(14)	-78 (2)	489 (1)	424 (4)
Cp(15)	-35 (2)	517 (2)	213 (4)
Cp(21)	-109 (2)	513 (2)	509 (3)
Cp(22)	-30 (1)	477 (1)	349 (4)
Cp(23)	-43 (2)	539 (2)	155 (3)
Cp(24)	-124 (3)	623 (3)	204 (5)
Cp(25)	-171 (1)	604 (1)	420 (5)
H(11)	-96	639	-1
H(12)	-222	709	329
H(13)	-200	575	643
H(14)	-57	429	525
H(15)	20	471	134
H(21)	-132	495	651
H(22)	21	413	385
H(23)	7	522	28
H(24)	-138	678	95
H(25)	-234	651	473

The structure of (II) was solved by Patterson and Fourier methods and refined by full-matrix least squares. A three-dimensional Patterson synthesis provided positions for W and Cl and confirmed the space group $P\bar{1}$. Three cycles of isotropic full-matrix least-squares refinement followed by two anisotropic cycles gave $R = 0.089$, with use of unit weights and minimization of $\sum w(|F_o| - |F_c|)^2$. A Fourier synthesis revealed the nitrosyl groups, and their inclusion in the refinement with anisotropic thermal parameters gave $R = 0.058$. A further Fourier synthesis contained peaks consistent with a disordered $(\eta^5\text{-C}_5\text{H}_5)_2$ ligand having two alternative configurations of similar weight. The C atoms of the two configurations were included in the model with 0.5 population parameters and isotropic temperature factors. Following three cycles of least squares, R was reduced to 0.032; all ten C atoms had similar, refined U values ($3.7\text{--}5.1 \text{ \AA}^2$). At this stage, the anomalous-dispersion corrections (Cromer & Liberman, 1970) for W and Cl were included along with an isotropic extinction parameter g (Becker & Coppens, 1974, 1975), and further refinement reduced R to

* Lists of thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34983 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0-026. A difference Fourier synthesis did not allow the (η^5 -C₅H₅) H atoms to be located, and their inclusion at calculated positions produced a wide variation of C—C distances (1.30–1.62 Å) which were less acceptable than those prior to their addition. Anisotropic refinement of the cyclopentadienyl C atoms also produced a worse geometry along with unacceptable thermal parameters. The refinement was concluded with three cycles of full-matrix least squares with anisotropic W, Cl, N, and O atoms and disordered (1:1) isotropic C atoms in the (η^5 -C₅H₅) rings. Scattering factors for all atoms were taken from Cromer & Mann (1968). The final value of R was 0.026 for the 2147 observed reflections, with $R_w = 0.029$. Unit weights appeared to be more acceptable than those derived from standard errors, the final standard deviation of an observation of unit weight (σ_1) being 1.10. The final value of g was $1.01(4) \times 10^4$, and mean and maximum parameter shifts in the last cycle were 0.004 and 0.022 e.s.d.'s, respectively. A final difference Fourier synthesis contained peaks of up to $\pm 0.9 \text{ e } \text{Å}^{-3}$ in the region of the heavy atoms, up to $\pm 0.5 \text{ e } \text{Å}^{-3}$ in the (η^5 -C₅H₅) region, and random fluctuations of up to $\pm 0.3 \text{ e } \text{Å}^{-3}$. Final atomic positional parameters are presented in Table 3.*

Discussion

The crystal structures of [$(\eta^5$ -C₅H₅)Cr(NO)₂Cl] (I) and [$(\eta^5$ -C₅H₅)W(NO)₂Cl] (II) consist of well separated arrays of discrete molecular units, the intermolecular distances generally corresponding to van der Waals contacts. The crystal packing for (II) is illustrated in Fig. 1. Both molecules are in 'piano-stool' con-

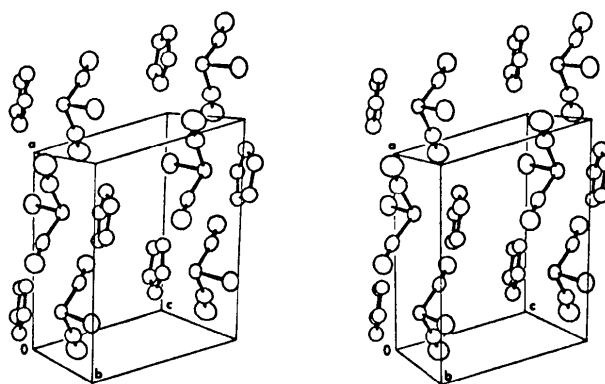


Fig. 1. Stereoscopic view of the crystal packing for [$(\eta^5$ -C₅H₅)W(NO)₂Cl]. Thermal ellipsoids are drawn at the 50% probability level with only one of the half-weight cyclopentadienyl rings shown.

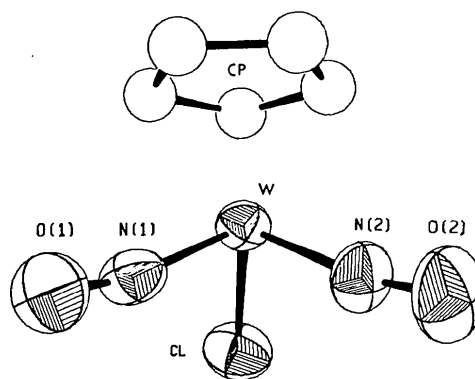


Fig. 2. Molecular structure of [$(\eta^5$ -C₅H₅)W(NO)₂Cl] with only one of the half-weight cyclopentadienyl rings shown. Thermal ellipsoids are drawn at the 50% probability level.

* See previous footnote.

Table 3. Final positional parameters for [$(\eta^5$ -C₅H₅)W(NO)₂Cl] (fractional $\times 10^3$; for W $\times 10^5$; for Cl, N and O $\times 10^4$) with estimated standard deviations in parentheses

	x	y	z
W	22871 (4)	33433 (5)	7169 (5)
Cl	1987 (4)	6474 (4)	1533 (5)
N(1)	3103 (9)	1731 (13)	2762 (13)
O(1)	3746 (10)	610 (14)	3766 (14)
N(2)	560 (9)	1921 (15)	2248 (14)
O(2)	-495 (10)	838 (17)	2996 (16)
Cp(11)	385 (3)	220 (3)	813 (3)
Cp(12)	431 (2)	441 (4)	764 (3)
Cp(13)	321 (3)	560 (3)	704 (3)
Cp(14)	207 (2)	428 (4)	721 (3)
Cp(15)	244 (3)	208 (4)	792 (4)
Cp(21)	250 (3)	526 (4)	696 (4)
Cp(22)	385 (3)	538 (4)	724 (4)
Cp(23)	431 (2)	340 (5)	784 (4)
Cp(24)	319 (3)	190 (3)	803 (4)
Cp(25)	212 (2)	316 (5)	741 (4)

figurations; the molecular structure of (II) is shown in Fig. 2. Bond distances and interbond angles for both complexes are given in Table 4. The geometrical parameters for (I) do not differ significantly from the values obtained previously from film data (Carter, McPhail & Sim, 1966), but they now have sufficiently small estimated standard deviations to permit a meaningful comparison with those of (II). In terms of their gross stereochemical features, the two molecules are isostructural. Furthermore, the geometries of the cyclopentadienyl and nitrosyl ligands are completely consistent with their functioning as five- and three-electron donors, respectively, to the metal centers in both (I) and (II).

The most chemically interesting comparison between the two structures involves the M —Cl bond distances. The Cr—Cl distance of 2.321 (1) Å is only 0.065 Å shorter than the W—Cl bond length of 2.386 (3) Å, whereas the average M —N and M —Cp distances are shorter by 0.108 and 0.164 Å, respectively, in the Cr complex. The relatively long Cr—Cl distance suggests somewhat greater ionic character for this linkage in (I),

Table 4. Bond distances (Å) and bond angles ($^\circ$) for $[(\eta^5\text{-C}_5\text{H}_5)_M(\text{NO})_2\text{Cl}]$ complexes

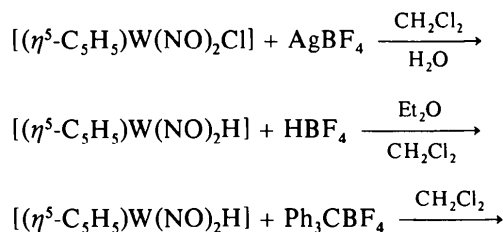
CP designates the unweighted centroid of the cyclopentadienyl ring. Cp designates a cyclopentadienyl carbon atom.

	(I) $M = \text{Cr}$	(II) $M = \text{W}$
$M\text{-Cl}$	2.321 (1)	2.386 (3)
$M\text{-N}(1)$	1.717 (3)	1.832 (9)
$M\text{-N}(2)$	1.717 (3)	1.819 (8)
$M\text{-CP}$	1.851	2.015
$\text{N}(1)\text{-O}(1)$	1.157 (4)	1.15 (1)
$\text{N}(2)\text{-O}(2)$	1.159 (4)	1.17 (1)
$M\text{-Cp}(11)$	2.24 (3)	2.33 (2)
$M\text{-Cp}(12)$	2.26 (2)	2.35 (2)
$M\text{-Cp}(13)$	2.22 (2)	2.37 (2)
$M\text{-Cp}(14)$	2.19 (1)	2.33 (2)
$M\text{-Cp}(15)$	2.12 (2)	2.32 (2)
$M\text{-Cp}(21)$	2.20 (2)	2.40 (2)
$M\text{-Cp}(22)$	2.17 (2)	2.39 (2)
$M\text{-Cp}(23)$	2.21 (2)	2.35 (2)
$M\text{-Cp}(24)$	2.14 (3)	2.32 (2)
$M\text{-Cp}(25)$	2.19 (1)	2.36 (2)
$\text{Cp}(11)\text{-Cp}(12)$	1.37 (2)	1.48 (3)
$\text{Cp}(12)\text{-Cp}(13)$	1.38 (2)	1.40 (3)
$\text{Cp}(13)\text{-Cp}(14)$	1.32 (3)	1.42 (3)
$\text{Cp}(14)\text{-Cp}(15)$	1.39 (3)	1.48 (3)
$\text{Cp}(15)\text{-Cp}(11)$	1.43 (6)	1.45 (3)
$\text{Cp}(21)\text{-Cp}(22)$	1.36 (2)	1.41 (3)
$\text{Cp}(22)\text{-Cp}(23)$	1.39 (3)	1.38 (3)
$\text{Cp}(23)\text{-Cp}(24)$	1.38 (4)	1.48 (3)
$\text{Cp}(24)\text{-Cp}(25)$	1.40 (3)	1.40 (3)
$\text{Cp}(25)\text{-Cp}(21)$	1.40 (3)	1.40 (3)
$\text{N}(1)\text{-M-N}(2)$	93.9 (1)	92.0 (4)
$\text{N}(1)\text{-M-Cl}$	99.3 (1)	102.2 (3)
$\text{N}(2)\text{-M-Cl}$	100.8 (1)	101.6 (3)
CP-M-Cl	116.8	115.0
$\text{CP-M-N}(1)$	121.6	120.1
$\text{CP-M-N}(2)$	119.7	121.8
$M\text{-N}(1)\text{-O}(1)$	170.0 (3)	168.4 (8)
$M\text{-N}(2)\text{-O}(2)$	168.8 (3)	169.0 (1.0)
$\text{Cp}(11)\text{-Cp}(12)\text{-Cp}(13)$	107 (3)	106 (2)
$\text{Cp}(12)\text{-Cp}(13)\text{-Cp}(14)$	110 (2)	110 (2)
$\text{Cp}(13)\text{-Cp}(14)\text{-Cp}(15)$	110 (1)	109 (2)
$\text{Cp}(14)\text{-Cp}(15)\text{-Cp}(11)$	105 (2)	105 (2)
$\text{Cp}(15)\text{-Cp}(11)\text{-Cp}(12)$	108 (3)	109 (2)
$\text{Cp}(21)\text{-Cp}(22)\text{-Cp}(23)$	110 (2)	108 (2)
$\text{Cp}(22)\text{-Cp}(23)\text{-Cp}(24)$	108 (2)	109 (2)
$\text{Cp}(23)\text{-Cp}(24)\text{-Cp}(25)$	107 (3)	104 (2)
$\text{Cp}(24)\text{-Cp}(25)\text{-Cp}(21)$	108 (2)	110 (2)
$\text{Cp}(25)\text{-Cp}(21)\text{-Cp}(22)$	107 (2)	108 (2)

which in the extreme can be represented as $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2]^+\text{Cl}^-$, an ionic complex containing a sixteen-electron organometallic cation. In contrast, the W-Cl distance implies the existence of a much more covalent bond, and (II) is thus best viewed as a neutral, eighteen-electron complex. Such an interpretation of the structural results is in accord with the observed properties of both complexes.

Both (I) and (II) are stable towards H_2O , but only (I) shows any appreciable solubility in this solvent. Treatment of the aqueous solution with AgBF_4 results in the ready formation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2]\text{BF}_4$, an

ionic complex which is soluble in H_2O and polar organic solvents and displays good air stability (Malito, 1976). On the other hand, attempts to prepare the analogous $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2]\text{BF}_4$ by any of the reactions



result in the formation of ill defined green oils. Tractable products are obtained only if these reactions are carried out in donor solvents such as CH_3CN and if the resulting reaction mixtures are treated with either neutral Lewis bases, L , or halide ions, X^- (Legzdins & Martin, 1979). The respective products obtained, namely $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2L]\text{BF}_4$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2X]$, reflect the tendency of W to attain the favored eighteen-electron valence configuration in complexes of this type.

Both (I) and (II) can be converted to $[(\eta^5\text{-C}_5\text{H}_5)\text{-M}(\text{NO})_2R]$ ($M = \text{Cr}$ or W ; $R = \text{alkyl}$ or aryl) complexes by treatment with AlR_3 reagents, but the conversions involving (II) require much longer reaction times and proceed in lower yields (Hoyano, Legzdins & Malito, 1975). Complex (I) is also alkylated by Grignard reagents, whereas (II) is not. These observations are consistent with the presence of a more easily cleaved M-Cl bond in (I).

A CH_2Cl_2 solution of (I) displays absorptions attributable to the nitrosyl ligands at 1816 and 1711 cm^{-1} in its infrared spectrum, whereas a CH_2Cl_2 solution of (II) exhibits $\nu(\text{NO})$ at 1733 and 1650 cm^{-1} (Legzdins & Malito, 1975). These spectral data indicate that retrodonative bonding of the metal atom to the nitrosyl groups occurs to a smaller extent in (I). This feature is in accord with the view that the metal center in (I) is more cationic in character than that in (II) and hence has less π -electron density available for $d\pi \rightarrow p\pi^*$ bonding with the NO ligands. The anomalous ^{15}N chemical shift observed for (I) (Botto, Kolthammer, Legzdins & Roberts, 1979) may also be a manifestation of the more positive character of the Cr atom. The physical and chemical properties of the molybdenum congener, $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})_2\text{Cl}]$, resemble more nearly those displayed by the tungsten complex, (II), thereby implying the existence of a principally covalent Mo-Cl bond.

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Ruthenium Ketoxime Complexes.

II. Structure of the Hydrated Barium Salt of Tris(dihydrogenviolurato)ruthenate(II)

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Abstract

$\text{Ba}^{2+}[\text{Ru}^{\text{II}}(\text{C}_4\text{H}_2\text{N}_3\text{O}_4)_3]_2 \cdot 9\text{H}_2\text{O}$, $\text{C}_{24}\text{H}_{12}\text{BaN}_{18}\text{O}_{24} \cdot \text{Ru}_2 \cdot 9\text{H}_2\text{O}$, is triclinic, space group $P\bar{1}$, with $a = 12.81(1)$, $b = 14.12(1)$, $c = 15.61(1)$ Å, $\alpha = 96.5(1)$, $\beta = 99.7(1)$, $\gamma = 122.1(1)^\circ$, $Z = 2$. The structure was refined to $R = 0.091$ ($R_w = 0.102$). The chelation of the divalent Ru is similar to that in $\text{H}_3\text{O}^+[\text{Ru}^{\text{II}}(\text{C}_4\text{H}_2\text{N}_3\text{O}_3)_3]^- \cdot 3\text{H}_2\text{O}$. The Ba atom is surrounded by nine O atoms forming a deformed tricapped trigonal prism.

Introduction

The reaction between *trans*- $\text{Na}_2[\text{Ru}(\text{OH})(\text{NO})(\text{NO}_2)_4]$ and barbituric acid ($\text{C}_4\text{H}_4\text{N}_2\text{O}_3$) in aqueous solution gives a deep-red complex which has been characterized by IR, ^1H NMR, and magnetic measurements as sodium tris(dihydrogenviolurato)ruthenate(II)

(Brémard, Muller, Nowogrocki & Sueur, 1977). The present salt is isolated in high yield (95%) from the reaction mixture by addition of the precipitating cation Ba^{2+} .

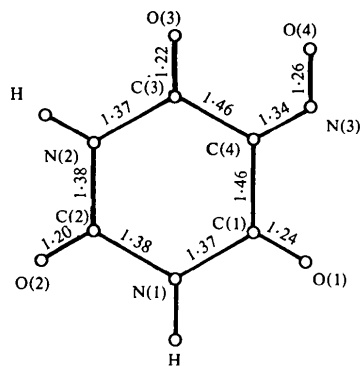


Fig. 1. Schematic structure and bond lengths (Å) of the dihydrogenviolurato ion in the hydrated potassium salt, with numbering scheme.