Spectroscopic Studies of a Square-pyramidal Nitridochromium(v) Complex

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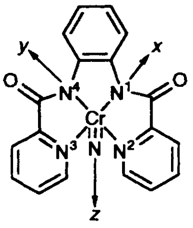
The ESR and UV/VIS spectra have been studied for solutions of [*N,N*'-bis(pyridine-2-carbonyl)-*o*-phenylenediamido]nitridochromium(v) having a square-pyramidal (CrN_5) chromophore. The *g* and ^{53}Cr hyperfine coupling tensors (*A*) are axially symmetric. An analysis of the *A* tensor indicated a $3d_{xy}$ ground-state Kramers doublet. Fairly high d_π–p_π interaction in the $Cr\equiv N$ formally triple bond was also revealed. The striking stability of this complex can be attributed to the remarkable d_π–p_π covalency of the $Cr\equiv N$ bond. None of the d–d* transitions has been observed in the region of $\lambda \geqslant 600$ nm at room temperature. Bands at 25 000 and 29 000 cm^{-1} have been tentatively assigned to charge-transfer transitions. The considerable difference between the $A_\perp(^{53}Cr)$, $a(^{53}Cr)$, $g_\perp$ and g_{iso} values of nitrido- and those of oxo-chromium(v) complexes have been explained in terms of the different extents of covalency in the $Cr\equiv N$ and $Cr=O$ multiple bonds.

Chromium(v) species have been identified as transient intermediates during the reduction of various chromyl(vi) (CrO_2^{2+}) complexes,[1] and a few chromium(v) complexes have actually been studied. Electron spin resonance studies have been reported for the majority of those complexes, of which the $Cr=O$ formal double bond is a common structural feature.[2–7] This bond may enable oxygen transfer to unsaturated organic compounds. Efforts to realize this possibility have been made successfully by using $[CrO(tpp)]^+$ (H_2tpp = 5,10,15,20-tetraphenylporphyrin) having a $CrON_4$ chromophore and $[CrO(salen)]^+$ [H_2salen = *N,N*'-bis(salicylidene)ethane-1,2-diamine] with a $CrO(cis\text{-}N_2O_2)$ one.[6,7] Spectroscopic and paramagnetic properties of chromium(v) halide oxide complexes, especially $[CrOCl_4]^-$, have been extensively studied experimentally as well as theoretically for more than three decades.[8–14] However, there is still controversy in the assignment of the charge-transfer (c.t.) bands, indicating that it is hard and complicated to investigate the electronic structure of this type of complexes.

Photochemical studies of azidochromium(iii) complexes[15] led to the first isolation of a nitridochromium(v) complex, [CrN(salen)].[16] Subsequently, surprisingly stable [CrN(ttp)] (H_2ttp = 5,10,25,20-tetra-*p*-tolylporphyrin) and [CrN(oep)] (H_2oep = 2,3,7,8,12,13,17,18-octaethylporphyrin) complexes were prepared and characterized,[17,18] while the related [CrO(tpp)]Cl was unstable and easily reduced to diamagnetic [CrO(tpp)] by CH_2Cl_2.[19] Diamagnetic nitridomanganese(v) porphyrinates are also very stable,[18] despite oxomanganese(v) porphyrinates being even more reactive than the oxochromium(v) porphyrinates.[20] Therefore, the nitrido complexes of the first transition metals are much more stable than the related oxo complexes. Recently Che *et al.*[21] prepared a third class of very stable nitridochromium complex, [*N,N*'-bis(pyridine-2-carbonyl)-*o*-phenylenediamido]nitridochromium(v), [CrN(L^1)], and reported its crystal structure. However, the chemistry of the nitridochromium complexes has received little attention to date, despite chromium(v) being one of the rare cations (Cr^V, Mo^V and Re^{VI}) to form isolable d^1 paramagnetic complexes of both oxo and nitrido type.

The complex [CrN(L^1)] has a N_5 donor set in a square-pyramidal co-ordination with the nitride ligand at the apical position. The axial bond distance of 1.56 Å is much shorter than the basal bond lengths (average 2.02 Å), suggesting a $Cr\equiv N$ triple bond.[21] This structure is similar to that of [CrN(ttp)].[17] The $3d^1$ electronic configuration for [CrN(L^1)] has been confirmed based on the μ_{eff} value of $1.93\mu_B$ ($\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}).[21] This complex has a dianionic carboxamide ligand in addition to the trivalent nitride anion, which neutralizes the highly positive charge on the central quinquevalent chromium cation to form the isolable complex. Actually this complex is stable not only thermally but also against photoirradiative excitations in view of the photo-oxidative preparation. It is of interest to determine the electronic structure of this complex and to investigate the differences between the electronic structures of the nitrido- and oxo-chromium complexes. This article describes the results of ESR and UV/VIS spectral measurements of [CrN(L^1)].



[CrN(L^1)]

Experimental

Sample Preparation.—The free ligand H_2L^1 was prepared by condensation between *o*-phenylenediamine and pyridine-2-carboxylic acid in the presence of triphenyl phosphite and was purified as long white needles by repeated recrystallization from chloroform solution.[22] The complex [CrN(L^1)] was prepared through the photo-oxidation of Na[Cr(L^1)(N_3)$_2$] in acetonitrile according to Che *et al.*[21] The crystals of [CrN(L^1)] were deposited during the photolysis and recrystallized from dimethylformamide (dmf)–MeCN.

The solvents dmf and MeCN were used in the UV/VIS measurements. The complex was dissolved in toluene–dmf (3:1) for the ESR measurements, then degassed by the freeze–pump–thaw procedure. A dmf solution was also prepared in order to investigate solvent effects, and was used without deaeration because a flat sample tube was employed for this high relative permittivity solvent. Owing to the poor solubility of the complex the acetonitrile solution did not afford a high enough signal-to-noise ratio to permit resolution of the parallel component of the hyperfine tensor ($A_{\parallel}$) due to the less abundant (9.54%) ^{53}Cr isotope. No other non-co-ordinating solvents could be found for the ESR measurements, because of lack of solubility.

In order to compare the UV/VIS spectra of $[\mathrm{CrN(L^1)}]$ with those of $[\mathrm{CuL^1(H_2O)}]$ and $[\mathrm{ZnL^1(H_2O)}]$, the last two complexes were prepared by the method of Chapman and Vagg.[23] The square-pyramidal co-ordination of $[\mathrm{CuL^1(H_2O)}]$ was previously established by X-ray crystallography.[24] Aqua[*N*,*N*′-bis(pyridine-2-carbonyl)trimethylenediamido]copper(II) dihydrate, $[\mathrm{CuL^2(H_2O)}]\cdot 2\mathrm{H_2O}$, was also prepared according to the reported procedure,[25] where $\mathrm{H_2L^2}$ was prepared by the same procedure as that for $\mathrm{H_2L^1}$.

Spectroscopic Measurements.—The UV/VIS spectra in the 240–900 and 800–1700 nm regions were recorded on Hitachi 320 and JASCO UVIDEC-590 spectrophotometers, respectively. A long-light-path cell (10 cm) was also used for the 500–900 nm region. The ESR spectra were recorded at ambient temperature and 77 K on a JEOL JES-ME-3X spectrometer equipped with 100 kHz field modulation. The magnetic field was calibrated by the splitting observed for Mn$^{\mathrm{II}}$ in MgO, which had previously been corrected by the splitting for Fremy's salt, $[\mathrm{K_2\{ON(SO_3)_2\}}]$, [$a$(N) = 1.300 mT and g = 2.0054].[26] The microwave frequencies were measured with a Takeda-Riken frequency counter. The resonant-field intensity was estimated from the spacing between the spectral line under consideration and the line from the lithium salt of tetracyanoquinodimethane (tcnq) taken as a secondary standard.

Results and Discussion

UV/VIS Spectra.—The UV/VIS spectrum of $[\mathrm{CrN(L^1)}]$ in dmf was in good accordance with that reported by Che *et al.*[21] The spectrum at 300–230 nm (in MeCN) is very similar to that of the $\mathrm{H_2L^1}$ free base [$\lambda_{\max}$ = 268 nm ($\varepsilon \approx$ 15 000 dm^3 mol^{-1} cm^{-1}) and a shoulder at about 285 nm]. No band or shoulder was detected in the range 500–1700 nm (detectable limit $\varepsilon \leqslant$ 1 dm^3 mol^{-1} cm^{-1}). The ε values at the tail of the low-energy c.t. band were 200 and 22 dm^3 mol^{-1} cm^{-1} at 500 and 590 nm, respectively. Therefore, the excitation energies for the allowed d–d* transitions are considered to be greater than 17 000 cm^{-1} (= 590 nm), while the $b_2 \longrightarrow e_{\pi}^*$ (d–d*) transitions of $[\mathrm{CrOCl_5}]^{2-}$ and $[\mathrm{CrOCl_4}]^-$ occur at 13 000 and 12 000 cm^{-1}, respectively.[8,12e,14,27]

Intense bands in MeCN solution were observed at 370 (ε = 6500), 290 (shoulder) and 267 nm (ε = 18 500 dm^3 mol^{-1} cm^{-1} carrying vibronic fine structure of 1300–1500 cm^{-1} separation), as shown in Fig. 1. The bands in dmf appeared at 375 (ε = 6600 dm^3 mol^{-1} cm^{-1}) and 290 nm. Gaussian decomposition of the spectra was carried out by using the SP program,[28] the region above 35 000 cm^{-1} being omitted (Fig. 2).

The component bands at 25 400 and 28 700 cm^{-1} in Fig. 2 were tentatively assigned to c.t. bands, since the estimated ε value of the latter weaker band is 3100 dm^3 mol^{-1} cm^{-1} which exceeds the acceptable level for a d–d* transition. The bands at 32 800 and 34 400 cm^{-1} may be mainly ascribed to transitions within the L^1 ligand, because similar bands were observed for $[\mathrm{CuL^1(H_2O)}]$, $[\mathrm{ZnL^1(H_2O)}]$ and $[\mathrm{CuL^2(H_2O)}]$. Comparing the Gaussian-resolved bands for the dmf solution with those for the MeCN solution, the proposed c.t. bands in the former showed a hypsochromic shift of 700–900 cm^{-1}.

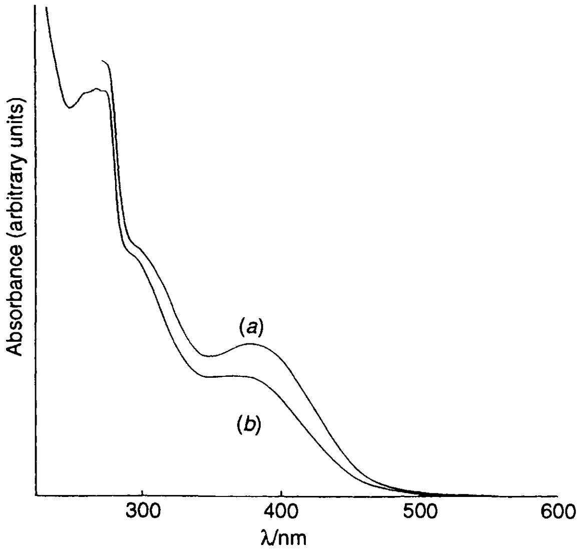


Fig. 1 Optical absorption spectra of the $[\mathrm{CrN(L^1)}]$ complex in dmf (*a*) and MeCN solution (*b*)

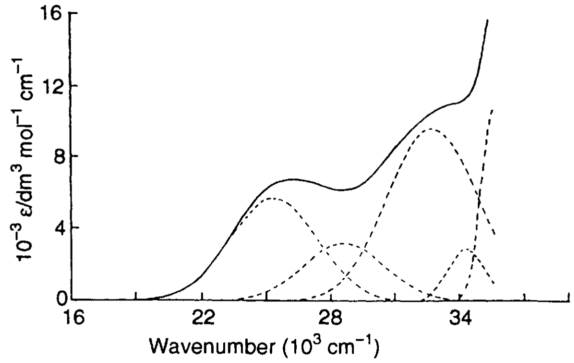


Fig. 2 Gaussian decomposition of the UV/VIS spectrum of $[\mathrm{CrN(L^1)}]$ in dmf solution

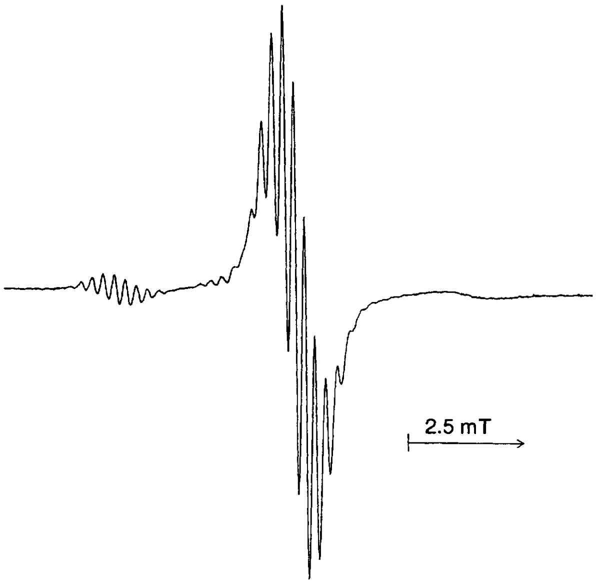


Fig. 3 The ESR spectrum of $[\mathrm{CrN(L^1)}]$ in toluene–dmf (3 : 1) solution at room temperature

ESR Spectra.—The ESR spectrum observed for the toluene–dmf (3:1) solution at room temperature exhibited a sharp isotropic signal at g_{iso} = 1.983 (Fig. 3), which indicates the 3d^1 ($S = \frac{1}{2}$) electronic configuration. This value is comparable with 1.982 for a dmf solution and 1.985 for a powder sample where the sixth co-ordination site is vacant. The isotropic spectrum displays an intense central resonance due to the chromium isotopes with I = 0. The central resonance is flanked by a satellite quartet hyperfine structure due to the less-abundant (9.54%) ^{53}Cr isotope with $I = \frac{3}{2}$. The isotropic hyperfine

Table 1 The ESR data for $[CrN(L^1)]$ and literature data for relevant complexes

	$[CrN(L^1)]$ in		Related complexes[a]				
	toluene–dmf (3 : 1)	dmf	**A**	**B**	**C**	**D**	**E**
g_{iso}	1.983	1.982	1.9825	1.982	1.988		
$a(^{53}Cr)$/mT	2.84	2.73	2.827[b]	2.3	1.94		
$\lvert a(N)\rvert$/mT	0.23	0.23	0.277	0.285			
$g_\perp$	1.992	1.992	1.9945		1.979	1.977	1.975
$g_\parallel$	1.956	1.956	1.9583		2.006	2.008	1.987
$\langle g\rangle$[c]	1.980	1.980	1.9824		1.988	1.987	1.979
$A_\perp(^{53}Cr)$/mT	2.21	2.19	2.24[b]			1.05	0.75[b]
$A_\parallel(^{53}Cr)$/mT	4.41	4.33	4.01[b]			3.84	3.87[b]
$\langle A\rangle$[c]/mT	2.94	2.90	2.83[b]			1.99	1.79[d]
Ref.	This work	This work	18	19	11	8	5

[a] **A**, [CrN(oep)]; **B**, $[CrO(tpp)]^+$; **C**, $[CrOCl_4]^-$; **D**, $[CrOCl_5]^{2-}$; **E**, $[CrO\{Et_2C(O)CO_2\}_2]^-$ (O=CrO_4 chromophore). [b] Sign not specified. [c] Calculated from the principal values. [d] The reported small anisotropy in A_x and A_y has been averaged; the sign was not given in the literature.

coupling constant of this isotope was estimated to be $|a(^{53}Cr)| = 2.84$ mT from the average of the spacings between the corresponding superhyperfine lines due to the $M_I = -\frac{3}{2}$ and $-\frac{1}{2}$ hyperfine transitions.

The low-field hyperfine absorptions carried a well resolved superhyperfine structure with 11 lines (Fig. 4), the expected intensity ratio for five equivalent nitrogen nuclei being 1:5:15:30:45:51:45···. A similar superhyperfine structure was reported for [CrN(ttp)] and [CrN(oep)].[17,18] However, it was not observed at the highest-field hyperfine absorption owing to the molecular tumbling rates.[29] The same effect was observed for bulky complexes such as [CrN(ttp)] and [CrN(oep)].[17,18] The 11-line superhyperfine structure reveals that the Fermi-contact interactions of all five nitrogen nuclei occur to the same extent in spite of the chemical non-equivalency and correspond to a spin density of 0.004 (=0.23/55.7) on each nitrogen, where 55.7 mT is the *a* value for an isolated nitrogen atom.[2]

The $|a(^{53}Cr)|$ value is dependent on the solvent (see Table 1). The considerable perturbation by the sixth ligand was also observed as a decrease in $|a(^{53}Cr)|$ from 2.3 mT for [CrO(tpp)]-Cl to 2.2 mT for $[CrO(tpp)(NH_2Bu^t)]Cl$.[19] Therefore, the same type of perturbation by the solvent molecule cannot be excluded in the present case.

The ESR measurements at 77 K revealed an axially symmetric system (Fig. 5). Therefore, we adopted C_{4v} local symmetry at the chromium site, which was tolerably consistent with that in the crystal. The spectrum gave $g_\perp = 1.992$ and $g_\parallel = 1.956$; the average is $\langle g\rangle = 1.980$ which is close to $g_{iso} = 1.983$ observed at room temperature. The same *g* tensors were observed for [CrN(ttp)] and [CrN(oep)].[17,18] The order of $g_\parallel < g_\perp$ seems plausible for the so-called less-than-half system. However, the reverse order ($g_\parallel > g_\perp$) was observed for $[CrO\{Et_2C(O)CO_2\}_2]^-$, $[CrOCl_5]^{2-}$ and $[CrOCl_4]^-$ complexes.[5,8,11]

The absorption at the lowest field in Fig. 5 can be ascribed to the perpendicular component of the *A* tensor due to the ^{53}Cr isotope, estimated as $|A_\perp(^{53}Cr)| = 2.21$ mT. The parallel component was also observed, $|A_\parallel(^{53}Cr)| = 4.41$ mT. The average is $\langle A\rangle = 2.94$ mT which is comparable with $|a(^{53}Cr)| = 2.84$ mT. The numerical discrepency between $\langle A\rangle$ and $|a(^{53}Cr)|$ can be attributed to the so-called pseudo-contact term which is associated with the Δg (see below).[2]

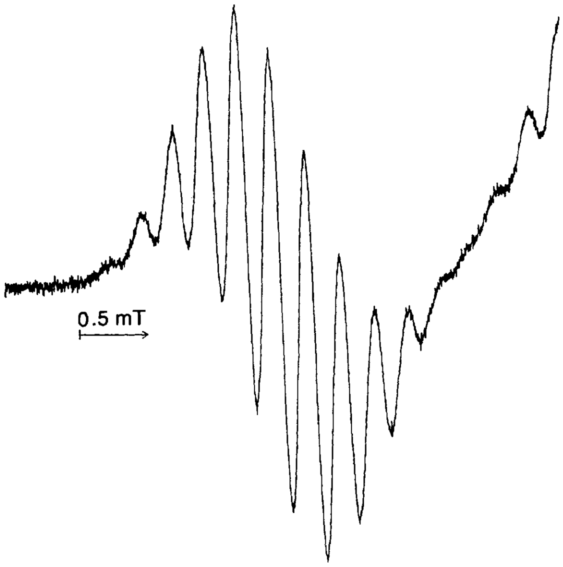


Fig. 4 Nitrogen superhyperfine structure observed in the low-field portion of the spectrum shown in Fig. 3

The Nature of the Cr≡N *Bond*.—To date the ground-state electronic configuration for nitridochromium complexes has been presumed to be $3d_{xy}$ similar to that used extensively for $3d^1$ oxometal complexes.[8,12–14,30–32] The *A* tensor will be useful to discuss the ground state electronic configuration. The dipolar coupling tensors (A^{zz}, A^{xx}, A^{yy}) due to the electron–nuclear dipolar interaction for the same atom are[2] $4P/7$, $-2P/7$, $-2P/7$ for half-filled d_{z^2}, $2P/7$, $-P/7$, $-P/7$ for half-filled d_{yz} and d_{xz}, and $-4P/7$, $2P/7$, $2P/7$ for half-filled $d_{x^2-y^2}$ and d_{xy} where *P* is defined as in equation (1) where $\langle r^3\rangle$ is

$$P = g\beta g_n\beta_n/\langle r^3\rangle \qquad (1)$$

the average of the cube of the distance from the nucleus to the half-filled *d* electron and the other symbols have their usual meanings. Since g_n of chromium is negative, the *P* value should be negative. On the other hand, the exchange polarization for the inner s spin affords an isotropic hyperfine coupling constant due to the Fermi-contact interaction,[2] since the α spin in the 3d orbital polarizes β spins in the region near the nucleus of the inner s orbitals [equation (2)]. When g_n is negative the

$$a = (8\pi/3)g\beta g_n\beta_n|\psi_s(0)|^2 \qquad (2)$$

isotropic hyperfine coupling constant is positive. Whatever 3d orbital is singly occupied, the condition of $a > 0$ and $P < 0$ consequently holds for the ^{53}Cr ion. For half-filled $d_{x^2-y^2}$ and d_{xy}, the simultaneous equations $A_\parallel(\text{obs.}) = -(4P/7) + a$ and $A_\perp(\text{obs.}) = (2P/7) + a$ give $P = -2.57$ mT and $a \approx \langle A\rangle = 2.94$ mT which is actually close to $|a(^{53}Cr)| = 2.84$ mT. The values adopted $A_\parallel$ and $A_\perp$ have positive sign. A similar procedure gives $P = -12.9$ and -25.7 mT for half-filled d_{z^2} and d_{xz} (d_{yz}) respectively. These values far exceed the limit for the Cr^{5+} free-ion state or $P_0 = -5.37$ mT.[2] Thus, the ESR

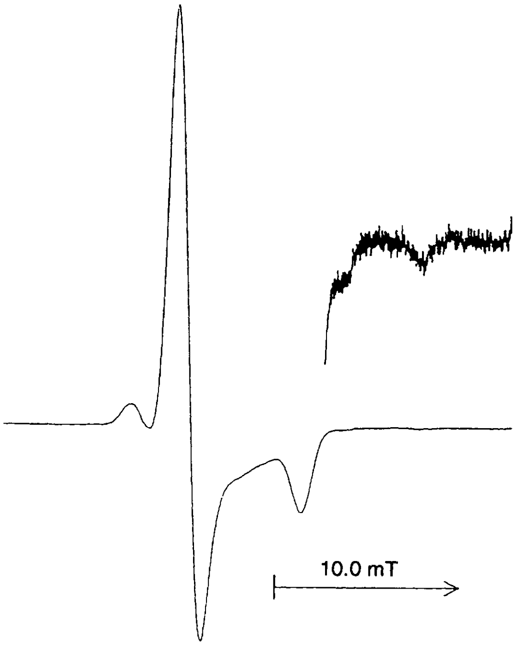


Fig. 5 The ESR spectrum of $[CrN(L^1)]$ in toluene–dmf (3:1) glassy solution at 77 K

studies indicate a $3d_{xy}$ ground-state Kramers doublet. Application of the same procedure to oxochromium complexes in Table 1 provides $\langle A \rangle = 1.99$ mT and $P = -3.26$ mT for **D**, and $\langle A \rangle = 1.79$ mT and $P = -3.64$ mT for **E** ($O{=}CrO_4$ chromophore).

The same conclusion can be drawn from McGarvey's crystal-field treatment[33] for the d_{xy}^1 configuration in a large tetragonal field compared to the spin–orbit coupling, because, since the contributions from the third and fourth terms in equations (3)

$$A_{\parallel} = P[-\kappa - (4/7) + (g_{\parallel} - g_e) + (3/7)(g_{\perp} - g_e)] \quad (3)$$

and (4) do not exceed 5% of the sums of the first and second

$$A_{\perp} = P[-\kappa + (2/7) + (11/14)(g_{\perp} - g_e)] \quad (4)$$

terms, the equations are almost equivalent to those used above. Here κ is the Fermi-contact term and $g_e = 2.0023$. Equations (5)

$$\langle A \rangle = (A_{\parallel} + 2A_{\perp})/3 = (-P\kappa) + (\langle g \rangle - g_e)P = a + (\langle g \rangle - g_e)P \quad (5)$$

and (6) derived from those above show the relationship between

$$\kappa = |a/P| \approx |\langle A \rangle/P| \quad [\text{when } (\langle g \rangle - g_e) \text{ is fairly small}] \quad (6)$$

$\langle A \rangle$ and a. Note that the thus estimated P values of the nitridochromium complexes in Table 1 are substantially smaller than those of the oxochromium complexes. More interestingly the κ values of the former complexes are larger than unity, while those of the latter are smaller than unity as anticipated for transition-metal complexes; κ = 1.14, 1.37, 0.61 and 0.49 for $[CrN(L^1)]$, $[CrN(oep)]$, $[CrOCl_5]^{2-}$ and $[CrO\{Et_2C(O)CO_2\}_2]^-$, respectively. Using the s orbital of a hydrogen-like atom, simplistic combination of equations (1) and (2) suggests that κ might increase with decrease in P or with increase in $\langle r^3 \rangle$ [equation (7)] where a_B is the Bohr radius. We

$$\kappa \propto \langle r^3 \rangle |\psi_s(0)|^2 \propto \langle r^3 \rangle / a_B^3 \quad (7)$$

can now postulate that the mean radius of the 3d orbitals in the nitridochromium complexes is larger than that in oxochromium ones.

The greater the covalency the more the 3d orbital expands (nephelauxetic effect). The a value of a metal ion decreases usually as the covalency increases.[2] Exchange polarization for 1s and 2s inner electrons by 3d α spin produces β spin at the nucleus. Since the 3s orbital is slightly more diffuse than the 3d orbitals or possesses outer s-orbital character, 3s α spin is polarized at the nucleus. The increasing covalency expands the 3d orbitals and lowers the effective charge on the metal ion with a resultant increase in a; associated slight orbital expansion of the inner s orbitals reduces the electron density at the nucleus and hence decreases a to a greater extent, so that in general the net result is a decrease in a as the covalency increases. Presumably this is the case with oxochromium complexes. For nitridochromium complexes the $\langle A \rangle$ and $a(^{53}Cr)$ values are much larger than those of the oxochromium ones in Table 1. A possible explanation for this is as follows. The remarkable expansion of the 3d orbitals of the $Cr{\equiv}N$ moiety probably diminishes the outer 3s-orbital character, so that the smaller cancellation of the α spin by the reduced β spin results in a larger a value. Goodings and Heine[34] carried out unrestricted Hartree–Fock (UHF) calculations in which they obtained a considerably larger hyperfine field than that of the free iron atom by using 3d orbitals expanded by about 5% at the maximum and 10% over the tail region. On the other hand, Sunil *et al.*[13] showed theoretically that the $\langle 1/r^3 \rangle$ or P value of the 3d orbital decreases linearly with increase in the number of 3d electrons. Therefore, since the effective number of 3d electrons on the chromium ion will be more in the $[Cr{\equiv}N]^{2+}$ than in the $[Cr{=}O]^{3+}$ moiety, the nephelauxetic effect in the former will be superior to that in the latter. The different extent of the nephelauxetic effect can probably be attributed to the difference between the formal charges of O^{2-} and N^{3-} and between the atomic electron affinities[35] of oxygen [141 ($O \longrightarrow O^-$), −780 kJ mol^{-1} ($O^- \longrightarrow O^{2-}$)] and nitrogen [−7 ($N \longrightarrow N^-$), −800 ($N^- \longrightarrow N^{2-}$) and −1290 kJ mol^{-1} ($N^{2-} \longrightarrow N^{3-}$)].

The highly covalent character of the $Cr{\equiv}N$ bond can be also inferred from molecular orbital (MO) theory. The unpaired electron occupies the b_2 MO [equation (8)] in C_{4v} symmetry[13]

$$\psi_{b_2} = \beta_1 d_{xy} - \beta_2(p_y^1 - p_x^2 - p_y^3 + p_x^4) \quad (8)$$

where d_{xy} represents the $3d_{xy}$ orbital of the chromium ion, and p_x and p_y the $2p_x$ and $2p_y$ orbitals of the designated nitrogen atoms. These 2p orbitals mainly contribute to the C–N–C σ bonds, so that this MO should have a highly non-bonding character. The theory of g and A tensors of transition-metal complexes is generally based on the perturbation method introduced by Abragam and Pryce[36] for the crystal-field model and later modified to include covalency effects.[37] Some references on this topic have appeared in ref. 13 where expressions (9) and (10) were presented based on a zero-

$$g_{\perp} = g_e - [2(\alpha_3\beta_1\lambda_M + 2\alpha_{10}\beta_2\lambda_L)(\alpha_3\beta_1 + 2\alpha_{10}\beta_2)]/\Delta E(b_2 \longrightarrow e_\pi{}^*) \quad (9)$$

$$A_{\perp} = P[(2\beta_1{}^2/7) - \kappa - (11/7)(\alpha_3\beta_1\lambda_M + 2\alpha_{10}\beta_2\lambda_L)\alpha_3\beta_1/\Delta E(b_2 \longrightarrow e_\pi{}^*)] \quad (10)$$

overlap model. Here α_3 and α_{10} are the metal $3d_{xz}$ ($3d_{yz}$) and ligand $2p_z$ orbital coefficients of the $e_\pi{}^*$ MO, respectively. The spin–orbit coupling constants for the metal 3d and ligand 2p orbitals are given by λ_M and λ_L, respectively. The more electrons the chromium ion has the smaller is its spin–orbit coupling constant.[38] Taking account of the calculation for $[CrOCl_4]^-$ by Sunil *et al.*,[13] the $(\alpha_{10}\beta_2)^2$ value may be much smaller than 0.01. To set $\alpha_{10}\beta_2$ in the above equations to zero results in expressions (11) and (12) corresponding to those

$$g_e - g_{\perp} = 2(\alpha_3\beta_1)^2\lambda_M/\Delta E(b_2 \longrightarrow e_\pi{}^*) \quad (11)$$

$$A_{\perp} = P[(2\beta_1{}^2/7) - \kappa - (11/7)(\alpha_3\beta_1)^2\lambda_M/\Delta E(b_2 \longrightarrow e_{\pi}{}^*)] \quad (12)$$

given by Kon and Sharpless[8] in which the integration has been limited to the metal atom. The $(g_e - g_{\perp})$ values of the nitridochromium complexes in Table 1 are much smaller than those of the oxochromium complexes. The $\Delta E(b_2 \longrightarrow e_{\pi}{}^*)$ values reported for $[CrOCl_4]^-$ and $[CrOCl_5]^{2-}$ are 13 500 [ref. 12(*a*)] and 13 000 cm^{-1},[8] respectively, while the corresponding transition in $[CrN(L^1)]$ cannot be observed below about 17 000 cm^{-1} at room temperature. This is consistent with the above ESR observations. The larger $\Delta E(b_2 \longrightarrow e_{\pi}{}^*)$ indicates a more extensive d_{π}–p_{π} interaction between the metal and apical nitrogen atom; consequently a smaller $\alpha_3{}^2$ value can be anticipated.

Equation (12) can be rewritten by using (11) to give (13).

$$A_{\perp} = (2/7)\beta_1{}^2P - P\kappa - (11/14)P(g_e - g_{\perp}) \quad (13)$$

Application of this equation to the data of $[CrN(L^1)]$ provides a $\beta_1{}^2P$ value of −2.3 mT which is close to that estimated (−2.57 mT) earlier. Semiempirical $\beta_1{}^2$ and P values for $[CrOCl_5]^{2-}$ are 0.87 and −3.8 mT, respectively,[8] and the corresponding squared coefficients calculated theoretically (atomic characters) for $[CrOCl_4]^-$ are 82[12b,13] and 95%.[12e] Assuming the $\beta_1{}^2$ value to be 0.8–0.9 for $[CrN(L^1)]$, the P value is estimated to be −2.9 to −2.6 mT which is still much smaller than those of the Cr^{5+} free ion and even $[CrOCl_5]^{2-}$.

The spin–orbit coupling constant of the complex is not always easy to estimate, because it is much dependent on the net charge of the atom under consideration. Values from 190 to 380 cm^{-1} were calculated for chromium having one to five electrons in the 3d shell.[13,38] The reported coupling constants for $[CrOCl_5]^{2-}$ and $[CrOCl_4]^-$ are 230 and 290 cm^{-1}, respectively.[8,13] Assuming $\Delta E(b_2 \longrightarrow e_{\pi}{}^*)$ to be 17 000 cm^{-1}, application of equation (11) to $[CrN(L^1)]$ gives $(\alpha_3\beta_1)^2$ values of 0.44 and 0.29 for λ_M = 200 and 300 cm^{-1}, respectively. Presuming the same $\beta_1{}^2$ value as above, $\alpha_3{}^2$ ranges from 0.32 to 0.55, while 0.81[8] was reported for $[CrOCl_5]^{2-}$ and the atomic characters of $[CrOCl_4]^-$ were 63,[13] 66[12b] and 80%.[12e] The atomic characters for the 3d orbital of chromium and the 2p orbital of oxygen in the bonding e_{π} MO of $[CrOCl_4]^-$ are 30 and 64%.[13] Therefore, we can estimate that the d–p π-bonding character in $[CrN(L^1)]$ is larger than that of the oxochromium complexes.

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