Synthesis and Structural Characterization of an Air-stable 17-Electron Complex containing the $\{Cr(NO)\}^{2+}$ Core†

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The reaction between $[Cr(bdmpam)(CO)_3]$ [bdmpam = bis(3,5-dimethylpyrazol-1-ylmethyl)-aminomethane] and an excess of $[NO][BF_4]$ in MeCN gives the air-stable 17-electron monomeric product $[Cr(bdmpam)(NO)(NCMe)_2][BF_4]_2$, which has been characterized by elemental analysis, i.r., e.s.r. spectroscopy, magnetic moment, and *X*-ray crystallography. The observed air stability of this paramagnetic monomer can be attributed to the presence of the bulky multidentate ligand bdmpam.

Though many paramagnetic acetonitrile complexes containing the $\{Cr(NO)\}^{2+}$ core are known,[1] no crystal structures have been reported. Ambiguities are usually encountered in the structural assignments concerning the σ or η^2 bonding mode of MeCN[2] and the linear or bent Cr–N–O linkage[3] in the complexes due to the similar ν(NO) and ν(CN) frequencies. We thus report here the synthesis and structural characterization of $[Cr(bdmpam)(NO)(NCMe)_2][BF_4]_2$ (**1**) [bdmpam = bis(3,5-dimethylpyrazol-1-ylmethyl)aminomethane]. This structure can serve as a good model for related paramagnetic $\{Cr(NO)\}^{2+}$ complexes.

It is also noteworthy that the observed air stability of the 17-electron species (**1**) constitutes a further example which supports the concept we reported earlier[4] that bulky multidentate ligands can help to stabilize paramagnetic compounds. We believe that this concept will facilitate the further development of organometallic radicals.[5]

Results and Discussion

The green air-stable product obtained from the reaction of $[Cr(bdmpam)(CO)_3]$[6] with an excess of $[NO][BF_4]$ in MeCN is not $[Cr(bdmpam)(CO)_3][BF_4]$ or $[Cr(bdmpam)(NO)(CO)_2][BF_4]$, but $[Cr(bdmpam)(NO)(NCMe)_2][BF_4]_2$ (**1**) based on the elemental analysis. This salt has a magnetic moment of 1.88 μ_B consistent with a single unpaired electron (*i.e.* low-spin Cr^I, d^5). Its e.s.r. spectrum in MeCN is similar to that[1c] of $[Cr(NO)(NCMe)_5][PF_6]_2$ (**2**), showing a single peak at g = 1.978 with no ligand hyperfine coupling. The two weak bands at 2 320 and 2 292 cm^{-1} with a similar intensity in the i.r. spectrum can be assigned to the two *cis* acetonitrile groups in (**1**) while the only strong band at 1 738 cm^{-1} is then assigned to the nitrosyl group. All these assignments are supported by the solid-state structure of this complex.

A view of the structure of the $[Cr(bdmpam)(NO)(NCMe)_2]^{2+}$ cation is presented in the Figure, which also shows the atomic labelling. From the Figure and the selected bond lengths and angles (Table 1) it is clear that the whole cation has approximate C_s symmetry with a mirror plane roughly containing the Cr atom and NO, while bisecting the bdmpam ligand and two *cis* acetonitriles. The Cr atom is in a nearly octahedral co-ordination environment with no η^2-acetonitriles. The bdmpam ligand adopts a facial mode around the metal atom. The fact that the nitrosyl group is *trans* to the central, saturated, nitrogen atom, N(3), rather than one of the other two terminal, unsaturated, nitrogen atoms, N(1) and N(5), probably reflects the π-acid property of NO. The bond angle Cr–N(6)–O is 174.9(12)°, not far from the expected 180°, indicating that the nitrosyl group can be considered as linear 'NO^+',[3] and found compatible with the first oxidation state assigned to the central metal atom in this 17-electron cationic radical. The Cr–N(nitrosyl) bond distance (1.65 Å) is comparable with the corresponding distances in the diamagnetic complexes *trans*-$[\{Cr(\eta\text{-}C_5H_5)(NO)(SPh)\}_2]$ (1.66 Å)[7] and $[\{Cr(\eta\text{-}C_5H_5)(NO)(NMe_2)\}_2]$ (1.63 Å).[8] Apparently, the bulky bdmpam ligand prevents the dimerization of (**1**) into the diamagnetic compound. It may also be true that the steric effects

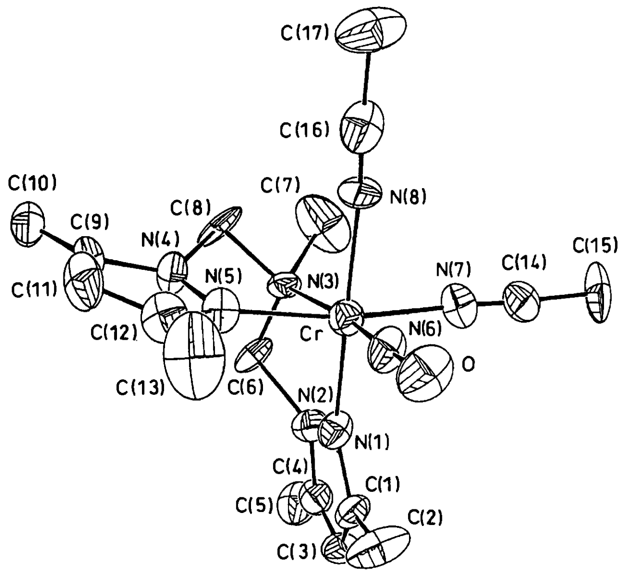

Figure. The molecular structure of the cation $[Cr(bdmpam)(NO)(NCMe)_2]^{2+}$, showing the atomic numbering scheme

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.

of this ligand restrict access to the central metal atom and (**1**) is air-stable while (**2**) is air-sensitive.

Experimental

The general operations and the spectral measurements were carried out as previously described.[4,9] The e.s.r. spectrum was obtained in solution at *X*-band frequency using a Bruker ER 200D-SRC spectrometer.

Synthesis.—[Cr(bdmpam)(NO)(NCMe)$_2$][BF$_4$]$_2$ (**1**). To a stirred solution of [Cr(bdmpam)(CO)$_3$][8] (0.38 g, 1.00 mmol) in MeCN (30 cm^3) was added solid [NO][BF$_4$] (0.35 g, 3.00 mmol). After gas evolution had ceased (10 min), the green solution was filtered and the solvent was removed under vacuum. The solid residue was recrystallized from CH$_2$Cl$_2$–MeOH to give the product (0.49 g, 84%). The solid is air-stable (Found: C, 34.65; H, 4.55; N, 18.95. Calc. for $C_{17}H_{27}B_2CrF_8N_8O$: C, 34.90; H, 4.65; N, 19.15%); $\mu_{eff.}$ = 1.88 μ_B [Evans method in (CD$_3$)$_2$CO, 21 °C]. I.r. (KBr): 2 320, 2 292 [ν(CN)] and 1 738 cm^{-1} [ν(NO)]. E.s.r. (MeCN, 21 °C): single peak at g = 1.978 with no ligand hyperfine coupling.

Table 1. Selected bond lengths (Å) and angles(°), with estimated standard deviations in parentheses

Cr–N(1)	1.999(11)	N(3)–C(7)	1.422(22)
Cr–N(3)	2.198(11)	N(6)–O	1.195(18)
Cr–N(5)	2.006(12)	N(7)–C(14)	1.147(24)
Cr–N(6)	1.648(13)	N(8)–C(16)	1.060(24)
Cr–N(7)	2.018(15)		
Cr–N(8)	1.993(12)		
N(1)–Cr–N(3)	79.6(5)	N(5)–Cr–N(6)	96.2(6)
N(1)–Cr–N(5)	95.9(5)	N(5)–Cr–N(7)	167.2(6)
N(1)–Cr–N(6)	98.2(6)	N(5)–Cr–N(8)	88.7(6)
N(1)–Cr–N(7)	88.1(5)	N(6)–Cr–N(7)	95.3(6)
N(1)–Cr–N(8)	167.4(6)	N(6)–Cr–N(8)	93.0(6)
N(3)–Cr–N(5)	78.7(5)	N(7)–Cr–N(8)	85.1(6)
N(3)–Cr–N(6)	174.1(6)	Cr–N(3)–C(7)	115.7(10)
N(3)–Cr–N(7)	90.1(5)	Cr–N(6)–O	174.9(12)
N(3)–Cr–N(8)	89.8(5)	Cr–N(7)–C(14)	177.7(14)
N(7)–C(14)–C(15)	177.2(19)	Cr–N(8)–C(16)	174.4(17)
N(8)–C(16)–C(17)	176.2(22)		

Crystallography.—*Crystal data*. $C_{17}H_{27}B_2CrF_8N_8O$, M = 585.05, orthorhombic, space group $P2_12_12_1$, a = 10.673(3), b = 13.502(3), c = 19.301(4) Å, U = 2 781.4 Å^3, Z = 4, D_c = 1.40 g cm^{-3}, F(000) = 1 196, Mo-K_α radiation (λ = 0.7107 Å), μ = 4.8 cm^{-1}.

The intensity data for a well defined crystal (0.22 × 0.30 × 0.50 mm) grown from CH$_2$Cl$_2$–hexane were measured at room temperature on an Enraf-Nonius CAD4 diffractometer. Up to $2\theta_{max.}$ of 50°, a total of 2 767 reflections were measured using the θ–2θ scan technique. Among these reflections, 1 332 were considered to be observed with $I \geqslant 2\sigma(I)$. The intensities were corrected for Lorentz polarization and absorption effects (calculated transmission range 0.76—1.00) using psi scans.[10]

Solution and refinement of the structure. All the structural analyses were performed on a VAX785 computer using the NRCVAX program.[10] The interpretation of the Patterson synthesis enabled the location of the Cr atom and the remaining non-hydrogen atoms were located from the subsequent Fourier syntheses. The two methylene groups, C(6) and C(8), of the bdmpam ligand were found to be disordered over two sites [occupancy of C(6), C(6′), C(8), and C(8′) 0.50]. All the non-hydrogen atoms were refined anisotropically while 23 hydrogen atoms were fixed at calculated positions. In order to keep an optimum ratio between the number of observed reflections and that of the variables used in the refinements, all the variables of boron and fluorine atoms and those of disordered carbon atoms were refined alternatively until the process converged. The maximum shift/error ratio of the final refinement was 0.255. In the last difference map the deepest hole was −0.33 e Å^{-3} and the highest peak was 0.43 e Å^{-3}; R = 0.069, R' = 0.078, goodness of fit = 2.85 based on F with $w = 1/\sigma^2(F_o)$.[9] Final positional parameters are listed in Table 2. A variable η[11] was tried during the least-squares refinement to check the chirality. However, the result was not clear-cut; this may be due to the fact that the anomalous dispersion effect from the Cr atom is not large enough (f' = 0.26 and f'' = 0.68) to distinguish the chirality.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Table 2. Final fractional atomic co-ordinates with estimated standard deviations in parentheses *

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cr	0.082 91(22)	0.150 84(15)	0.084 80(12)	C(9)	−0.179 4(14)	−0.035 7(12)	0.002 1(10)
N(1)	−0.031 2(11)	0.262 3(8)	0.110 6(6)	C(10)	−0.268 7(16)	−0.110 0(12)	0.019 9(9)
N(2)	−0.112 2(12)	0.241 8(9)	0.163 5(7)	C(11)	−0.141 3(18)	−0.001 3(17)	−0.059 1(9)
N(3)	−0.045 5(11)	0.074 2(8)	0.155 8(6)	C(12)	−0.058 7(17)	0.074 5(14)	−0.049 1(9)
N(4)	−0.112 0(12)	0.016 3(10)	0.050 0(7)	C(13)	0.007 8(22)	0.134 7(20)	−0.100 8(9)
N(5)	−0.035 7(11)	0.086 4(10)	0.017 9(6)	C(14)	0.253 8(15)	0.214 7(13)	0.211 1(9)
N(6)	0.166 8(11)	0.209 4(10)	0.026 0(7)	C(15)	0.333 5(15)	0.241 8(17)	0.269 6(9)
N(7)	0.192 6(13)	0.189 5(11)	0.165 5(7)	C(16)	0.242 9(17)	−0.035 5(15)	0.072 9(10)
N(8)	0.189 5(11)	0.029 8(9)	0.080 3(8)	C(17)	0.322 4(20)	−0.127 7(13)	0.067 1(12)
O	0.234 0(13)	0.253 7(10)	−0.012 6(7)	B(1A)	−0.003 7(24)	0.717 0(12)	0.119 6(9)
C(1)	−0.051 0(13)	0.358 9(11)	0.098 1(7)	F(1A)	0.095 7(14)	0.656 9(11)	0.134 4(5)
C(2)	0.013 8(22)	0.408 3(12)	0.039 4(11)	F(2A)	−0.048 0(11)	0.765 9(7)	0.172 4(6)
C(3)	−0.134 9(16)	0.394 3(11)	0.142 5(10)	F(3A)	−0.085 8(16)	0.651 7(9)	0.100 1(7)
C(4)	−0.174 3(15)	0.323 7(12)	0.184 2(8)	F(4A)	0.020 2(14)	0.770 2(9)	0.068 2(6)
C(5)	−0.262 0(16)	0.320 7(12)	0.241 7(9)	B(1B)	0.465(3)	0.542(3)	0.277 7(22)
C(6)	−0.151(3)	0.132 4(20)	0.163 4(17)	F(1B)	0.439 6(19)	0.471 6(14)	0.335 0(10)
C(6′)	−0.087(4)	0.154 3(24)	0.208 6(15)	F(2B)	0.367 7(18)	0.518 0(19)	0.256 7(10)
C(7)	0.012 2(20)	0.020 6(18)	0.210 6(11)	F(3B)	0.451 9(15)	0.616 2(11)	0.326 3(10)
C(8)	−0.074(4)	−0.019 5(18)	0.122 3(15)	F(4B)	0.573 2(13)	0.525 7(10)	0.277 9(12)
C(8′)	−0.164(3)	0.051(3)	0.121 4(13)				

* Occupancy of C(6), C(6′), C(8), and C(8′) 0.50.

Acknowledgements

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