The Versatility of the Dihydrogenobis(1-pyrazolyl)borate Ligand, $H_2B(pz)_2^-$: Novel Anionic Complexes with Chromium(II), Chromium(III), and Manganese(II). *X*-Ray Structure of $[AsPh_4][MnCl\{H_2B(pz)_2\}_2]$ *

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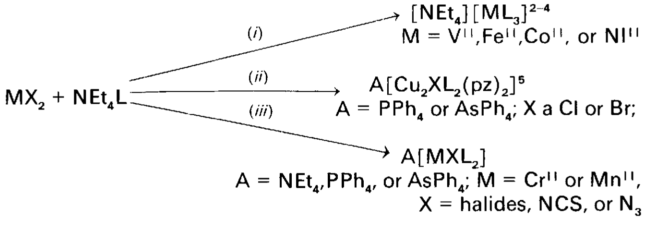
New five-co-ordinate chromium(II) and manganese(II) complexes with the ligand dihydrogenobis(1-pyrazolyl)borate, $H_2B(pz)_2$, have been prepared and characterized. The complexes have the general formula $A[MX\{H_2B(pz)_2\}_2]$ (M = Cr^{II} or Mn^{II}; A = NEt_4, PPh_4, or $AsPh_4$; X = halides or pseudohalides). All of the complexes are high spin. The structure of $[AsPh_4][MnCl\{H_2B(pz)_2\}_2]$ has been determined by single-crystal *X*-ray diffraction methods. The compound crystallizes in the space group $P2_1/n$ with $a = 16.952(4)$, $b = 13.039(3)$, $c = 17.331(4)$ Å, $\beta = 105.53(2)°$, and $Z = 4$. The structure was solved by heavy-atom methods and refined to $R = 0.058$. The co-ordination geometry about manganese(II) is square pyramidal with the four donor N atoms of the two $H_2B(pz)_2$ ligands forming the basal plane and the Cl atom occupying the apical position. The Mn atom is displaced by 0.52 Å from the base of the pyramid toward the Cl atom. Slow oxidation of $[NEt_4][Cr\{H_2B(pz)_2\}_2(NCS)]$ in solution yields the chromium(III) complex $[NEt_4][Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]$ with co-ordinated ethoxo groups.

The dihydrogenobis(1-pyrazolyl)borate anion, $H_2B(pz)_2^-$, is a remarkable bidentate ligand first reported by Trofimenko and co-workers[1] to give neutral bis chelates, $[M\{H_2B(pz)_2\}_2]$, with first-row bivalent transition metals. The formation in the solid state of four-co-ordinate complexes, rather than being dictated by steric or electronic requirements of the ligand seems to be a consequence of the polar solvents employed (water or ethanol) where the neutral complexes are the least-soluble species. Complexes having different stoicheiometries from that referred to above may be obtained if suitable reaction conditions are adopted (see Scheme).[2–5]

Now we report on chromium(II) and manganese(II) complexes having the general formula $A[MX\{H_2B(pz)_2\}_2]$ (M = Cr^{II}, X = Cl or Br, A = PPh_4 or $AsPh_4$; X = I or NCS, A = NEt_4; M = Mn^{II}, X = Cl, A = PPh_4 or $AsPh_4$; X = NCS or N_3; A = NEt_4). The *X*-ray structure of the five-co-ordinate complex $[AsPh_4][MnCl\{H_2B(pz)_2\}_2]$ has been determined. To date the number of crystal structures of five-co-ordinate manganese(II) complexes is limited.[6–9] The synthesis and structural characterization of manganese complexes with pyrazole-derived ligands may contribute to a better understanding of the structure and reactivity of active sites in biological systems. An ethoxo complex of chromium(III), namely $[NEt_4][Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]$, obtained by oxidation of $[NEt_4][Cr\{H_2B(pz)_2\}_2(NCS)]$ in MeCN–EtOH solution, is also reported.

Experimental

Materials and Preparations.—All reagents and solvents used were of reagent-grade purity. All preparative operations on both chromium(II) and manganese(II) complexes were carried out under a nitrogen atmosphere using conventional Schlenk-line techniques.



Scheme. L = $H_2B(pz)_2^-$. (*i*) EtOH; (*ii*) EtOH, Me_2CO, AX; (*iii*) EtOH, AX

The salt $K[H_2B(pz)_2]$[1] and chromium(II) salts[10] were prepared by the literature methods. Ethanol solutions of $Cr(NCS)_2$, $Mn(NCS)_2$, and $Mn(N_3)_2$ were prepared by metathetical reactions of the metal chlorides with either NaNCS or NaN_3. Ethanol solutions of $[NEt_4][H_2B(pz)_2]$ were prepared immediately before use by metathetical reaction of $K[H_2B(pz)_2]$ and NEt_4Cl.

The complexes were all prepared at room temperature with ethanol as solvent using the same synthetic procedure. Solutions of $[NEt_4][H_2B(pz)_2]$ (3×10^{-3} mol in 20 cm^3 of ethanol) and PPh_4X (X = Cl or Br) or $AsPh_4Cl$ (10^{-3} mol in 10 cm^3 of ethanol) were subsequently added to a solution (20 cm^3) of the appropriate metal salt (10^{-3} mol). Crystalline compounds were obtained by leaving the solutions to stand overnight at room temperature under a nitrogen current. The tetraethylammonium complexes were obtained similarly without the addition of either PPh_4X or $AsPh_4Cl$. The solid compounds were washed with warm benzene to remove any traces of neutral bis chelates, then with ethanol and diethyl ether, and finally dried in a nitrogen current at 60 °C. Complexes of adequate purity were thus obtained (Table 1).

The complex $[NEt_4][Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]$ was obtained by leaving a dilute solution of $[NEt_4][Cr\{H_2B(pz)_2\}_2(NCS)]$ in a MeCN–EtOH mixture to stand overnight at about 50 °C in a stream of nitrogen containing traces of O_2. The complex can be recrystallized from a MeCN–EtOH mixture (Table 1).

Crystals of $[AsPh_4][MnCl\{H_2B(pz)_2\}_2]$ suitable for *X*-ray

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* Tetraphenylarsonium chlorobis[dihydrogenobis(1-pyrazolyl)borato]manganate(II).

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

Table 1. Characterization of the complexes[a]

Complex	Analysis[b] (%)					$\mu_{eff.}$ (295 K)	$\Lambda_M{}^c$/ohm^{-1} cm^2 mol^{-1}	Spectroscopic data	
	C	H	N	As/P	Cr/Mn			State[d]	$\lambda_{max.}$/nm (ε/cm^2 mmol^{-1})
$[AsPh_4][CrClL_2]$	56.3	4.75	14.4			4.82	120	d.r.	590
	(56.5)	(4.75)	(14.7)						560(46)
$[AsPh_4][CrBrL_2]$	53.8	4.55	13.7	8.90	6.40	4.83	117	d.r.	555
	(53.4)	(4.50)	(13.8)	(9.25)	(6.45)				550(40)
$[PPh_4][CrBrL_2]$	56.6	4.85	14.6	3.90	6.70	4.77	118	d.r.	560
	(56.5)	(4.75)	(14.6)	(4.05)	(6.80)				545(44)
$[NEt_4][CrIL_2]$	39.7	6.20	20.5		8.50	4.93	177	d.r.	545
	(39.8)	(6.00)	(20.9)		(8.60)				535(48), 390(27)
$[NEt_4][Cr(NCS)L_2]$	46.7	6.75	25.7		9.70	4.85	155	d.r.	530(sh)
	(47.2)	(6.80)	(26.2)		(9.75)				530(sh), 390(sh)
$[NEt_4][Cr_2(EtO)_3(NCS)_2L_2]$[e]	43.2	6.55	19.7		13.4	2.85[f]	57	d.r.	538, 400(sh), 350(sh)
	(43.1)	(6.60)	(19.8)		(13.3)				538(32), 405(44), 362(54)
$[AsPh_4][MnClL_2]$[g]	55.8	4.70	14.4			6.01	140		430(sh), 280(sh), 271(5 270)
	(56.3)	(4.75)	(14.6)						264(5 811), 215(52 000)
$[PPh_4][MnClL_2]$	59.3	4.55	15.3			5.94	122		430(1.5), 276(3 478)
	(59.7)	(5.00)	(15.5)						268(4 203)
$[NEt_4][Mn(NCS)L_2]$	46.5	6.75	25.8		10.8	5.91	130		430(sh), 274(2 790)
	(47.0)	(6.75)	(26.1)		(10.2)				262(6 980)
$[NEt_4][Mn(N_3)L_2]$	46.1	7.30	31.7		10.3	5.95	141		435(1.5), 215(sh)
	(46.1)	(6.95)	(32.3)		(10.5)				200(30 400)

[a] $L = H_2B(pz)_2$. [b] Calculated values in parentheses. [c] For *ca.* 5×10^{-3} mol dm^{-3} solutions in MeCN. Reference values are: $AsPh_4Cl$, 124; NEt_4Cl, 129 ohm^{-1} cm^2 mol^{-1}. [d] d.r. = Diffuse reflectance; otherwise, acetonitrile solution, *ca.* 5×10^{-3} mol dm^{-3}. [e] S, 8.15 (8.25); O, 5.95 (6.15%). [f] Average value for metal atom. [g] Cl, 4.50 (4.60%).

analysis were obtained by slow evaporation of a CH_2Cl_2–EtOH solution of the reactants at about 40 °C under a nitrogen atmosphere.

Methods.—Conductance and spectrophotometric measurements on the complexes in solution were performed in suitable airtight containers (u.v., i.r., and conductance cells) filled with a prepurified (oxisorb^R, Messer Griesheim) nitrogen atmosphere. The concentrations of the solutions were in the range (1—5) × 10^{-3} mol dm^{-3}. Spectrophotometric measurements were carried out with a Perkin-Elmer 238 i.r. spectrophotometer and with a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer. Conductivity data were obtained with a WTW model LBR/B conductance bridge. Magnetic measurements were performed on solid samples at room temperature by the Faraday method using a DMS-5 automated magnetometer.

Crystal Structure Determination of $[AsPh_4][MnCl\{H_2B(pz)_2\}_2]$.—*Crystal data.* $C_{36}H_{36}AsB_2ClMnN_8$, $M = 767.68$, monoclinic, space group, $P2_1/n$ (alternative setting of space group no. 14, ref. 11), $a = 16.952(4)$, $b = 13.039(3)$, $c = 17.331(4)$ Å, $\beta = 105.53(2)°$, $U = 3\,691(1)$ Å^3, $Z = 4$, $D_c = 1.381$ g cm^{-3}, $F(000) = 1\,572$, μ(Mo-K_α) = 13.4 cm^{-1}.

Data collection. A needle-shaped colourless crystal (0.15 × 0.20 × 0.70 mm) was mounted on an Enraf-Nonius CAD4 diffractometer [λ(Mo-K_α) = 0.710 69 Å, graphite monochromator]. Unit-cell parameters were determined from least-squares refinement of 24 reflections having $24 < 2\theta < 28°$. The intensities of *hkl* and $\bar{h}kl$ reflections in the 2θ range 5—46° were measured in the ω—2θ scan mode with a scan width $(1.10 + 0.34 \tan\theta)°$ and variable (2—8° min^{-1}) scan speed. Three standard reflections measured every 6 000 s showed no appreciable decay. Out of 5 160 reflections measured 2 700 having $I > 3\sigma(I)$ were used in subsequent calculations. Intensity data were corrected for Lorentz and polarization effects and, at isotropic convergence after the structure was solved, they were also corrected for absorption by an empirical procedure.[12] Calculations were performed on an IBM 4361; the principal computer programs used in the crystallographic calculations are listed in refs. 13—16. Scattering factors for the neutral atoms and the anomalous dispersion corrections for As and Mn were taken from ref. 17.

Structure solution and refinement. The positions of the heaviest atoms were provided by direct methods; those of the other non-hydrogen atoms were determined by a set of Fourier maps. In the full-matrix least-squares refinement the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized, where $w = [\sigma^2(F_o) + 0.0005F_o{}^2]^{-1}$. In the final cycles, anisotropic thermal parameters were assigned to the As, Mn, and Cl atoms, whereas all other atoms were refined isotropically. Although the positions of most H atoms were revealed by ΔF maps, these were introduced in calculated positions with E–H 1.00 Å (E = C or B) and $U_H = 1.2U_C$. In the final cycle (212 parameters the largest shift/error ratio <0.01) gave $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.058$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{\frac{1}{2}} = 0.060$. Extreme values of residual electron density in the final ΔF Fourier were 0.69 and -0.43 e Å^{-3}.

Atomic co-ordinates are listed in Table 2 and selected bond lengths and angles in Table 3.

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

Results and Discussion

The tetra-alkylammonium salt of the bidentate ligand dihydrogenobis(1-pyrazolyl)borate, $[NEt_4][H_2B(pz)_2]$, gives anionic complexes with both chromium(II) and manganese(II) which can be crystallized as salts of the bulky cations $AsPh_4{}^+$, $PPh_4{}^+$, or $NEt_4{}^+$. The general formula of the complexes is $A[MX\{H_2B(pz)_2\}_2]$ (M = Cr, X = Cl or Br, A = PPh_4 or $AsPh_4$; X = I or NCS, A = NEt_4; M = Mn, X = Cl, A = PPh_4 or $AsPh_4$; X = NCS or N_3, A = NEt_4). The chromium(II) complexes are stable in the solid state under an inert atmosphere but are extremely sensitive to oxidation when dissolved in MeCN. This meant that all of the operations on chromium(II) solutions were extremely difficult. The manganese(II) complexes are much more stable towards aerial oxidation. The magnetic moment values of the complexes are

Table 2. Atomic co-ordinates (× 10^4) for $[AsPh_4][MnCl\{H_2B(pz)_2\}_2]$*

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
As	148(1)	2 421(1)	3 294(1)	C(23)	−660(5)	−616(7)	3 052(6)
Mn	4 474(1)	2 317(1)	3 296(1)	C(24)	−926(5)	−747(8)	3 717(6)
Cl	3 353(1)	2 465(2)	4 090(1)	C(25)	−890(6)	27(7)	4 257(6)
N(1)	5 418(4)	1 214(5)	3 864(4)	C(26)	−575(5)	979(7)	4 134(5)
N(2)	6 233(4)	1 396(5)	4 045(4)	C(31)	−717(5)	3 392(6)	3 024(5)
N(3)	5 414(4)	3 495(5)	3 853(4)	C(32)	−532(5)	4 394(6)	2 821(5)
N(4)	6 231(4)	3 324(5)	4 009(4)	C(33)	−1 151(6)	5 083(7)	2 598(5)
N(5)	3 957(4)	3 363(5)	2 283(4)	C(34)	−1 951(6)	4 817(7)	2 542(5)
N(6)	3 889(4)	3 041(6)	1 526(5)	C(35)	−2 126(7)	3 838(8)	2 735(6)
N(7)	3 881(4)	1 074(5)	2 449(4)	C(36)	−1 512(6)	3 102(8)	2 969(6)
N(8)	3 846(4)	1 159(6)	1 656(5)	C(41)	624(5)	2 361(6)	2 417(5)
C(1)	6 634(6)	564(7)	4 437(6)	C(42)	104(6)	2 455(7)	1 655(5)
C(2)	6 090(6)	−137(8)	4 538(6)	C(43)	423(7)	2 436(8)	999(7)
C(3)	5 339(6)	286(7)	4 168(5)	C(44)	1 248(6)	2 312(7)	1 109(6)
C(4)	6 620(7)	4 186(8)	4 392(6)	C(45)	1 772(6)	2 225(7)	1 856(6)
C(5)	6 068(7)	4 864(9)	4 474(7)	C(46)	1 462(5)	2 252(6)	2 523(6)
C(6)	5 311(6)	4 433(8)	4 145(6)	C(51)	878(5)	2 808(6)	4 290(5)
C(7)	3 407(6)	3 713(8)	1 014(7)	C(52)	1 606(6)	2 318(8)	4 578(6)
C(8)	3 183(6)	4 461(8)	1 447(6)	C(53)	2 135(7)	2 619(8)	5 318(7)
C(9)	3 532(6)	4 230(7)	2 255(6)	C(54)	1 913(7)	3 393(8)	5 737(7)
C(10)	3 367(6)	389(8)	1 257(7)	C(55)	1 184(7)	3 865(9)	5 472(7)
C(11)	3 112(7)	−165(8)	1 778(7)	C(56)	650(6)	3 583(7)	4 725(6)
C(12)	3 430(6)	250(7)	2 531(6)	B(1)	6 583(7)	2 366(8)	3 739(7)
C(21)	−307(5)	1 109(6)	3 446(5)	B(2)	4 279(8)	2 025(10)	1 358(9)
C(22)	−349(5)	334(7)	2 896(6)				

* In this and the following table, estimated standard deviation in the least significant digit(s) are in parentheses.

Table 3. Selected bond distances (Å) and angles (°) for $[AsPh_4]$-$[MnCl\{H_2B(pz)_2\}_2]$

Mn–Cl	2.373(2)	Mn–N(5)	2.211(7)
Mn–N(1)	2.180(7)	Mn–N(7)	2.236(7)
Mn–N(3)	2.239(7)		
Cl–Mn–N(1)	108.5(2)	N(1)–Mn–N(5)	148.5(3)
Cl–Mn–N(3)	101.8(2)	N(1)–Mn–N(7)	88.0(3)
Cl–Mn–N(5)	103.0(2)	N(3)–Mn–N(5)	90.2(3)
Cl–Mn–N(7)	100.7(2)	N(3)–Mn–N(7)	157.5(3)
N(1)–Mn–N(3)	84.6(2)	N(5)–Mn–N(7)	85.0(3)

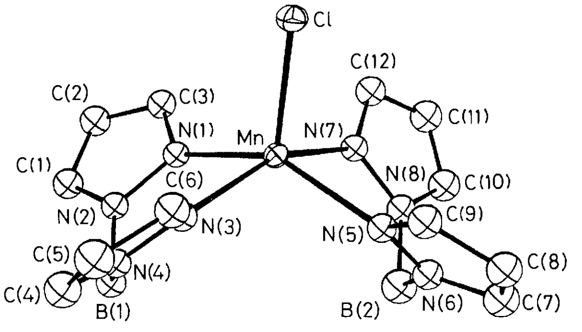

Figure. Structure of the anion $[MnCl\{H_2B(pz)_2\}_2]^-$

consistent with high-spin $S = 2$ [d^4, chromium(II)] and $S = \frac{5}{2}$ [d^5, manganese(II)] configurations (Table 1).

The slow oxidation of a MeCN–EtOH solution of the complex $[NEt_4][Cr\{H_2B(pz)_2\}_2(NCS)]$ in a stream of N_2 containing traces of O_2 led to the chromium(III) complex $[NEt_4][Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]$ containing co-ordinated ethoxo groups.

An *X*-ray structural investigation on the manganese(II) complex $[AsPh_4][MnCl\{H_2B(pz)_2\}_2]$ was carried out, as it could also provide information on the co-ordination geometry of the other complexes of the $[MX\{H_2B(pz)_2\}_2]^-$ series.

Manganese(II) *Complexes*.—The reflectance spectra of the complexes are similar to each other and are essentially featureless except for a continuously increasing absorption with decreasing wavelengths which makes the *d–d* transitions, expected to be very weak, hardly detectable or unobservable. The spectra of the complexes dissolved in MeCN exhibit a weak absorption band or shoulder (ε = 1—4 cm^2 mmol^{-1}) in the range 420—435 nm. Very intense bands are present below 300 nm which can be assigned as either intraligand [200—210 nm, ε = (3—5) × 10^4 cm^2 mmol^{-1}] or charge transfer [260—290 nm, ε = (3—4) × 10^3 cm^2 mmol^{-1}]. These spectral features are not unexpected for manganese(II) complexes with pyrazolylborate ligands[1,18] but are not informative about the stereochemistry or the co-ordination number of the $[MnX\{H_2B(pz)_2\}_2]^-$ species. Solutions of the present complexes in MeCN are relatively inert toward aerial oxidation and their electronic spectra remain substantially unchanged after the solutions are flushed with oxygen for 24 h at room temperature.

Crystal Structure of $[AsPh_4][MnCl\{H_2B(pz)_2\}_2]$.—The structure of $[AsPh_4][MnCl\{H_2B(pz)_2\}_2]$ consists of $AsPh_4^+$ cations and $[MnCl\{H_2B(pz)_2\}_2]^-$ anions in which the manganese atom is co-ordinated by the four N donor atoms and by one Cl atom (Figure). The co-ordination geometry is square pyramidal, with the Mn atom displaced by 0.52 Å from the best plane through the N atoms, which define the base of the pyramid, toward the Cl atom, which lies in the apical position. The Mn–Cl bond deviates by 2.6(1)° from the normal to the above least-squares plane. The Mn–N distances, 2.18—2.24 Å, are longer than those (2.11—2.16 Å) formed by the pyrrole nitrogens in porphyrin complexes with similar co-ordination geometries to that of the present compound.[7,8] They are also longer than the distances (2.11—2.13 Å) formed by the four imine N atoms of a macrocyclic ligand in another high-spin square-pyramidal manganese(II) complex.[9] Also the Mn–Cl distance in the present compound [2.373(2) Å] is longer than that [2.295(3) Å] found for a porphyrin derivative with the N_4Cl donor set.[7]

We can assume that all of the manganese(II) complexes reported here have in the solid state a structure substantially similar to that of $[AsPh_4][MnCl\{H_2B(pz)_2\}_2]$, mainly on the basis of their identical stoicheiometries.

Chromium Complexes.—In view of the identical stoicheiometries of the chromium(II) and manganese(II) complexes and of spectral properties of the former (see below), one can assign a square-pyramidal geometry also to the chromium(II) complexes. The reflectance spectra of the chromium(II) complexes are similar to each other and exhibit one asymmetric band in the range 530—590 nm with a broad and poorly resolved shoulder on the low-energy tail of the main band (Table 1). The main absorption is characteristically shifted towards higher energies in the order Cl, Br, I, which is opposite to the order of increasing ligand-field strength of the anions. Such spectral features are typical of tetragonally distorted (C_{4v}) chromium(II) complexes[19] and are in agreement with the proposed geometry.

The electronic spectra of the complexes in MeCN solution do not deviate substantially from those of the solid compounds and are distinctly different from the spectrum of square-planar $[Cr\{H_2B(pz)_2\}_2]$.[3] However, the extreme sensitivity of the dissolved complexes to aerial oxidation does not allow accurate investigations in solution. In this connection, the band or shoulder at about 390 nm in the electronic spectra of the complexes with the NEt_4^+ counter ion is indicative of the presence of appreciable amounts of chromium(III) species in solution. The exceptionally rapid oxidation of the present chromium(II) complexes in solution may be related to the co-ordinative unsaturation of the square-pyramidal geometry which allows a dioxygen molecule to approach the metal atom from the side of the sixth, unoccupied, co-ordination site of an octahedron. In one case a pure and reproducible crystalline compound could be obtained, by allowing the $[NEt_4][Cr\{H_2B(pz)_2\}_2(NCS)]$ complex dissolved in a MeCN–EtOH solution slowly to oxidize in a stream of N_2 containing traces of O_2. The complex thus obtained has the formula $[NEt_4][Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]$. A strong band at 1 095 cm^{-1} in its i.r. spectrum, which is not present in the spectrum of the $[NEt_4][Cr\{H_2B(pz)_2\}_2(NCS)]$ parent compound, is assigned to the C–O stretching frequency of the ethoxo group.[20] The magnetic moment for each chromium(III) atom is 2.85 μ_B at 293 K, well below the normal value for magnetically dilute chromium(III) species, thus suggesting a bi- or poly-nuclear structure. We tentatively assign to the chromium(III) complex a binuclear structure with three bridging ethoxides. Efforts to grow crystals of this complex failed because a new compound resulted which did not show any i.r. absorption attributable to the BH_2 stretching frequency of the ligand.

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