Structural and Magnetic Characterisation of the Compound $[NEt_4][Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]$ (pz = 1-pyrazolyl),* a Binuclear Complex of Chromium(III) with Three Bridging Ethoxo Groups

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The crystal and molecular structure of $[NEt_4][Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]$ [$H_2B(pz)_2$ = dihydrobis(1-pyrazolyl)borate] has been determined by single-crystal X-ray diffraction methods. The crystals are monoclinic, space group $P2_1$, with a = 9.561(9), b = 15.826(4), c = 12.979(3) Å, β = 93.06(8)° and Z = 2. The complex anion consists of two chromium(III) ions in chemically identical and approximately octahedral environments. The metal ions are bridged by three ethoxo groups. The co-ordination around each metal is completed by two N atoms of a $H_2B(pz)_2$ ligand and by the N atom of a NCS anion. The temperature dependence of the magnetic susceptibility of the compound has been determined in the range 8–280 K. The exchange interaction between the two chromium(III) ions was found to be antiferromagnetic with J = 87.0(2) cm^{-1} and the exchange Hamiltonian is $H = JS_1 \cdot S_2$.

We have recently reported novel anionic complexes of chromium(II) and manganese(II), formed by the dihydrogenobis(1-pyrazolyl)borate anion, $H_2B(pz)_2^-$, having 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 = halide or pseudohalide).[1] The chromium(II) derivatives, at variance with those of manganese(II), are quickly oxidised even in the presence of traces of oxygen. In one case the oxidation of a chromium(II) derivative gave a pure and reproducible crystalline compound of chromium(III) which was formulated as $[NEt_4][Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]$ on the basis of the elemental analysis.[1]

Now we report on the crystal and molecular structure and magnetic properties of this dinuclear, ethoxo-bridged, complex of chromium(III). Chromium(III) derivatives with co-ordinated alkoxides are not uncommon[2,3] but mixed-ligand complexes with three bridging ethoxides have not been structurally characterised, to the best of our knowledge.

Experimental

Details on the procedures and the materials employed in the synthesis of the complex $[NEt_4][Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]$ have been reported elsewhere, together with elemental analysis, spectrophotometric, conductivity and room-temperature magnetic data.[1] Crystals suitable for X-ray analysis were obtained by slow evaporation of a MeCN–BuOH solution of the complex at room temperature.

Magnetic Measurements.—The magnetic susceptibility of a microcrystalline sample of the complex was measured in the temperature range 8–280 K by the Faraday method using an AZTEC Informatique DMS-5 automated magnetometer equipped with an Oxford Instruments CF2000 cryostat. Diamagnetic corrections were carried out according to ref. 4.

X-Ray Structure Determination.—*Crystal data.* $C_{28}H_{51}B_2Cr_2N_{11}O_3S_2$, M = 779.5, monoclinic, space group $P2_1$ (no. 4), a = 9.561(9), b = 15.826(4), c = 12.979(3) Å, β = 93.06(8)°, U = 1961(2) Å^3 [by least-squares refinement of 20 automatically centred reflections ($12 \leqslant \theta \leqslant 13°$), λ = 0.710 69 Å], Z = 2, D_c = 1.320 g cm^{-3}, approximate dimensions 0.13 × 0.4 × 0.5 mm, $F(000)$ = 820, μ(Mo-Kα) = 6.8 cm^{-1}.

Data collection and processing. The red crystals were of regular prismatic form. Data were collected at room temperature with an Enraf-Nonius CAD4 diffractometer, in the ω–2θ mode with (1.10 + 0.35 tanθ)° scan width, variable scan speed 3–8° min^{-1} and graphite-monochromated Mo-Kα radiation. Of 3755 reflections ($\pm h, k, l$; $2.5 \leqslant \theta \leqslant 25°$), 3376 were unique and 2724 having $I > 3\sigma(I)$ were used in the final refinement. The intensities of three standard reflections measured periodically were constant throughout data collection. An empirical absorption correction[5] was applied at isotropic convergence, after the structure had been solved (maximum, minimum corrections 1.16, 0.76). Among the low-angle reflections no correction for secondary extinction was deemed necessary. The principal computer programs used in the crystallographic calculations are listed in refs. 5–7.

Structure analysis and refinement. The structure was solved by direct methods. A series of Fourier and Fourier difference maps yielded the positions of all non-hydrogen atoms. During the full-matrix least-squares refinement the y co-ordinate of one Cr atom was not allowed to refine, due to the polar nature of the space group. The position of the methyl carbons of two ethyl groups in the anion and one in the cation were found to be affected by disorder, each of these groups being distributed between two orientations. In the final least-squares cycles, in which the population parameters for the alternative positions were allowed to refine, the sites of each pair were assigned an overall isotropic thermal parameter and were constrained to form a unique C–C bond length with the respective methylene carbon atom. All the other non-hydrogen atoms were assigned anisotropic thermal parameters. Hydrogen atoms were introduced in calculated positions (C–H 0.96, B–H 1.06 Å) each with a thermal parameter *ca.* 20% larger than the $U_{equiv.}$ of the corresponding C or B atom. The H atoms of the disordered ethyl groups were assigned fractional

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* Tetraethylammonium tri-μ-ethoxo-bis{thiocyanato[dihydrobis(1-pyrazolyl)borato]chromate(III)}.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Atomic coordinates for $[NEt_4][Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]$[a]

Atom	*x*	*y*	*z*
Cr(1)[b]	0.2614(1)	0.3980	0.7093(1)
Cr(2)	0.3208(1)	0.4083(1)	0.5100(1)
S(1)	0.2149(4)	0.1403(2)	0.8945(3)
S(2)	0.3880(3)	0.1909(2)	0.2668(3)
O(1)	0.2836(6)	0.4917(4)	0.6153(4)
O(2)	0.4281(6)	0.3638(3)	0.6331(4)
O(3)	0.1594(6)	0.3588(4)	0.5797(4)
N(1)	0.0844(7)	0.4505(5)	0.7650(6)
N(2)	0.0763(7)	0.4841(6)	0.8610(6)
N(3)	0.3796(7)	0.4539(5)	0.8266(5)
N(4)	0.3329(8)	0.4833(6)	0.9163(5)
N(5)	0.1959(8)	0.4653(5)	0.3978(5)
N(6)	0.2406(8)	0.5044(6)	0.3134(5)
N(7)	0.4922(7)	0.4714(5)	0.4598(5)
N(8)	0.4982(8)	0.5106(6)	0.3672(6)
N(9)	0.2438(8)	0.2910(6)	0.7874(6)
N(10)	0.3515(9)	0.3104(6)	0.4200(6)
N(11)	0.7884(8)	0.3074(6)	0.1027(7)
C(1)	−0.0294(9)	0.4785(8)	0.7090(8)
C(2)	−0.1096(11)	0.5275(8)	0.7681(10)
C(3)	−0.0420(10)	0.5298(8)	0.8638(10)
C(4)	0.5115(9)	0.4802(7)	0.8207(7)
C(5)	0.5526(10)	0.5248(7)	0.9103(7)
C(6)	0.4366(10)	0.5255(7)	0.9678(7)
C(7)	0.0584(9)	0.4821(7)	0.4034(7)
C(8)	0.0163(11)	0.5340(8)	0.3192(8)
C(9)	0.1294(12)	0.5449(9)	0.2660(8)
C(10)	0.6066(9)	0.4955(7)	0.5166(7)
C(11)	0.6870(10)	0.5496(8)	0.4618(9)
C(12)	0.6144(10)	0.5585(7)	0.3678(8)
C(13)	0.2310(9)	0.2294(7)	0.8330(7)
C(14)	0.3659(9)	0.2590(6)	0.3553(8)
C(15)	0.2815(17)	0.5771(8)	0.6250(11)
C(16)	0.2953(16)	0.6324(9)	0.5484(12)
C(17)	0.4974(9)	0.2828(7)	0.6358(9)
C(181)[c]	0.5923(15)	0.2710(13)	0.7195(11)
C(182)[d]	0.6413(10)	0.2939(16)	0.6316(18)
C(19)	0.1045(10)	0.2759(7)	0.5651(9)
C(201)[e]	−0.0330(12)	0.2674(13)	0.6020(14)
C(202)[f]	0.0112(18)	0.2586(16)	0.4779(13)
C(21)	0.7563(13)	0.3758(9)	0.1810(13)
C(22)	0.7208(13)	0.3437(11)	0.2838(9)
C(23)	0.6633(13)	0.2522(9)	0.0791(11)
C(24)	0.5353(13)	0.2965(10)	0.0338(11)
C(25)	0.9094(12)	0.2531(10)	0.1400(11)
C(26)	1.0454(12)	0.3008(12)	0.1764(12)
C(27)	0.8323(13)	0.3513(9)	−0.0001(12)
C(281)[g]	0.8651(18)	0.2944(12)	−0.0832(13)
C(282)[h]	0.8008(27)	0.4369(12)	0.0319(25)
B(1)	0.1835(12)	0.4571(11)	0.9521(9)
B(2)	0.3891(13)	0.4937(10)	0.2748(9)

[a] In this and the following table estimated standard deviations on the least significant digit(s) are in parentheses. Atoms N(11) and C(21)–C(282) belong to the cation, all the other atoms to the complex anion. [b] The *y* coordinate of Cr(1) was not refined, due to the polar nature of the space group. [c] Atomic position affected by disorder, site with population parameter (p.p.) 0.583(3). [d] p.p. = 0.417(3). [e] p.p. = 0.572(3). [f] p.p. = 0.428(3). [g] p.p. = 0.814(3). [h] p.p. = 0.186(3).

Table 2 Selected bond distances (Å) and angles (°) for $[NEt_4][Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]$

Cr(1)–O(1)	1.939(6)	Cr(2)–O(1)	1.946(6)
Cr(1)–O(2)	1.994(5)	Cr(2)–O(2)	1.982(6)
Cr(1)–O(3)	1.998(6)	Cr(2)–O(3)	1.991(5)
Cr(1)–N(1)	2.052(7)	Cr(2)–N(5)	2.043(8)
Cr(1)–N(3)	2.048(7)	Cr(2)–N(7)	2.054(7)
Cr(1)–N(9)	1.985(8)	Cr(2)–N(10)	1.972(9)
Cr(1) · · · Cr(2)	2.683(2)		
O(1)–Cr(1)–O(2)	77.2(2)	O(1)–Cr(2)–O(2)	77.3(2)
O(1)–Cr(1)–O(3)	76.9(2)	O(1)–Cr(2)–O(3)	76.9(2)
O(2)–Cr(1)–O(3)	82.3(2)	O(2)–Cr(2)–O(3)	82.8(2)
N(1)–Cr(1)–N(3)	89.7(3)	N(5)–Cr(2)–N(7)	90.3(3)
N(1)–Cr(1)–N(9)	94.1(3)	N(5)–Cr(2)–N(10)	91.4(3)
N(3)–Cr(1)–N(9)	92.7(3)	N(7)–Cr(2)–N(10)	92.7(3)
O(1)–Cr(1)–N(9)	171.3(3)	O(1)–Cr(2)–N(10)	170.9(3)
O(2)–Cr(1)–N(1)	168.7(3)	O(2)–Cr(2)–N(5)	171.6(3)
O(3)–Cr(1)–N(3)	170.2(3)	O(3)–Cr(2)–N(7)	170.5(3)
Cr(1)–O(1)–Cr(2)	87.4(2)	Cr(1)–O(2)–Cr(2)	84.9(2)
Cr(1)–O(3)–Cr(2)	84.5(2)		

population parameters, linked to those of the appropriate images of the groups. The anomalous dispersion corrections for Cr and scattering factor data for the neutral atoms were from ref. 8. Refinement on 444 parameters, with the weighting scheme $w = [\sigma^2(F_o) + 0.005F_o^2]^{-1}$, converged at $R = 0.068$, $R' = 0.072$. The final ΔF map showed two maxima of heights ≈ 1.7 e Å^{-3} aligned with the metal atom positions, which could not be assigned any chemical significance.

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

Results and Discussion

The slow oxidation of a MeCN–EtOH solution of the five-co-ordinate chromium(II) complex $[NEt_4][Cr\{H_2B(pz)_2\}_2(NCS)]$,[1] in a stream of N_2 containing traces of O_2, affords a pure and reproducible chromium(III) complex which can be formulated, on the basis of the elemental analysis, as $[NEt_4][Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]$. The oxidation of the starting chromium(II) complex is accompanied by the formation of ethoxo species which co-ordinate to chromium(III), as well as by decomposition of part of the ligand.

We have already found that nickel(II),[9] cobalt(II)[9] or copper(II)[10] complexes containing co-ordinated $H_2B(pz)_2^-$ anions may be susceptible to ligand decomposition in an ethanol–acetone solution, thereby forming pyrazolate anions that co-ordinate to the metal atom. In the present case the formation of ethoxo species may result from EtOH attack on an intermediate oxidation product of $[Cr\{H_2B(pz)_2\}_2(NCS)]^-$, presumably a mono- or di-nuclear complex of chromium(III) containing co-ordinated oxygen. We have previously isolated an oxo-bridged chromium(III) complex, formed by slow oxidation of a polypyrazolyl chromium(II) complex.[11] It should be noted that the manganese(II) complexes $[MnX\{H_2B(pz)_2\}_2]^-$,[1] which are quite similar to those of chromium(II) but are stable towards aerial oxidation, do not give ethoxo derivatives under the experimental conditions in which the chromium(II) compounds do.[1] On the other hand a bis-methoxo-bridged complex of copper(II) with a polypyridyl ligand has been obtained by oxidation of the corresponding copper(I) complex with dioxygen in methanol suspension.[12]

Description of the Structure.—Atomic coordinates for the compound $[NEt_4][Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]$ are given in Table 1 and selected bond distances and angles in Table 2. A view of the dimetal anion is shown in Fig. 1. Each metal atom is in an approximately octahedral environment formed by the three O atoms of the bridging ethoxo groups, by the two N donor atoms of a $H_2B(pz)_2$ ligand anion and by the N atom of a thiocyanate anion. The N and O donor atoms span opposite faces of the octahedron about each metal atom; the O atoms,

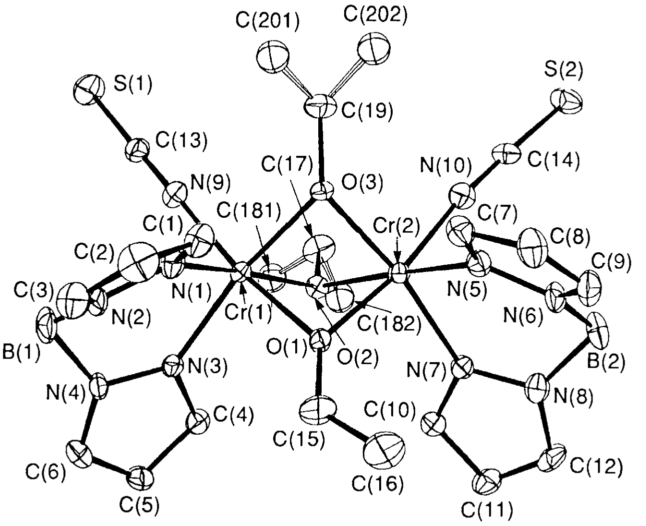

Fig. 1 View of the $[Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]^-$ anion. Both positions for the disordered methyl groups of two EtO^- ligands are shown.

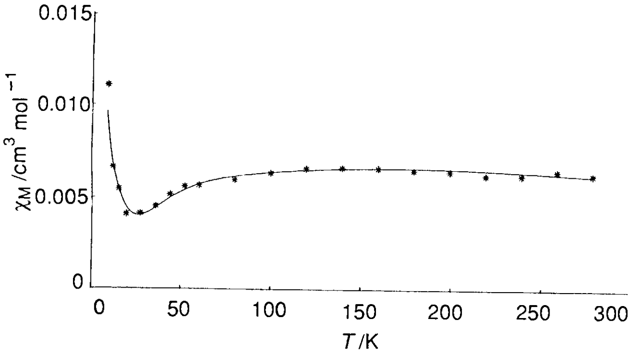

Fig. 2 Magnetic susceptibility data for $[NEt_4][Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]$. (*), Experimental points; (——), the best fit of the theoretical expression of a pair of exchange-coupled chromium(III) ions. Best-fit parameters are given in the text.

forming the inner layer in the dimetal unit, are in staggered positions with respect to the N atoms, which form the outer layers. The Cr and B atoms, those of the NCS groups, as well as those of the ethoxo group formed by O(1), all lie on one plane (within 0.08 Å), which forms a 90.9(2)° angle with the best plane through the four donor N atoms of the pyrazole groups. The methyl C(16) position in the above ethoxo group which is sheltered by a ligand cavity, is not affected by disorder, at variance with the other methyl groups in the anion and one in the cation which are affected by two-fold orientational disorder. The O(1) atom, lying in *trans* position with respect to the NCS anions, forms shorter bond distances to the metal atoms (by 0.05 Å, mean) than do the other two O atoms, which lie *trans* to the N atoms of the $H_2B(pz)_2$ ligands. The Cr–O distances formed by O(1) are in the range of those found for other alkoxo-bridged chromium(III) dimers,[13,14] whereas the distances formed by the other two O atoms in the present structure lie slightly outside that range. The Cr–N distances involving the NCS nitrogens, as well as those formed by the pyrazole N atoms, are slightly shorter (respectively by 0.03 and 0.05 Å, mean) than similar distances existing in the structure of the chromium(III) oxo-bridged dimer $[\{Cr(tpea)(NCS)\}_2O][BPh_4]_2$, where tpea is the tetradentate ligand tris(2-pyrazol-1-ylethyl)amine.[11]

Magnetic Measurements.—The temperature dependence of the molar magnetic susceptibility of $[NEt_4][Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]$ in the temperature range 8–280 K is shown in Fig. 2. It is indicative of an antiferromagnetic coupling between the two chromium(III) ions with a Curie-like tail at low temperatures due to a small amount of paramagnetic impurities.

The exchange interactions between the two chromium(III) ions can be described using a spin Hamiltonian of the form

$$H = JS_1{\cdot}S_2 + j(S_1{\cdot}S_2)^2 \qquad (1)$$

(1):[15] where J is the isotropic exchange coupling constant, j is the biquadratic coupling constant and $S_1 = S_2 = \frac{3}{2}$. Since in chromium(III) dimers $|j/J|$ is generally smaller than 0.1, j was neglected in the calculation of the energy levels in order to reduce the number of parameters needed to fit the magnetic data. Using the Van Vleck equation to compute the molar magnetic susceptibility and the isotropic Zeeman effect, the expression (2) was obtained. The magnetic susceptibility values

$$\chi_M = \frac{(Ng^2\mu_B{}^2/kT)(2e^{-J/kT} + 10e^{-3J/kT} + 28e^{-6J/kT})}{(1 + 3e^{-J/kT} + 5e^{-3J/kT} + 7e^{-6J/kT})} \qquad (2)$$

to be compared with the experimental ones can thus be computed by equation (3) where $\chi_M{}^{Cr}$ takes into account the

$$\chi_M{}^c = \chi_M(1 - \rho) + 2\chi_M{}^{Cr}\rho \qquad (3)$$

paramagnetic impurities and can be computed by use of equation (4) and ρ is the molar fraction of the impurities.

$$\chi_M{}^{Cr} = Ng^2\mu_B{}^2/3kT[S(S + 1)];\ S = \tfrac{3}{2} \qquad (4)$$

Equation (3) was employed to fit the magnetic susceptibility data using a Simplex minimisation routine. The function to be minimised was (5) where $\chi_M{}^o$ is the observed value of the

$$F = \Sigma(\chi_M{}^o - \chi_M{}^c)^2 \qquad (5)$$

magnetic susceptibility and the sum is over all the experimental temperatures. The quality of the fitting was judged using the usual R value [equation (6)]. The best fit was obtained with the

$$R = \Sigma||\chi_M{}^o| - |\chi_M{}^c||/\Sigma|\chi_M{}^o| \qquad (6)$$

parameters $g = 1.90(1)$, $J = 87.0(2)$ cm^{-1} and $\rho = 0.012(4)$. The final R value was 0.03.

In a number of chromium(III) dimers containing a Cr_2O_2 bridging network the energy separation between the singlet and the triplet levels originating from the exchange interaction, $\Delta E = J$, was found to be correlated to the ratio between the Cr–O–Cr bond angle (Φ) and the Cr–O bond length (r).[16] This correlation was rationalised using a molecular-orbital treatment.[17] A similar correlation between singlet–triplet splittings and the Φ to r ratio has been observed also for halide- and sulphur-bridged copper(II) systems.[18] By assuming that the same correlation also holds for the triply bridged dimers of chromium(III), which are still rare, we compute for $[Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]^-$ an average Φ/r value of 43.4° Å^{-1} which is close to the 42.6° Å^{-1} reported for $[Cr_2(OH)_3L_2][ClO_4]_3{\cdot}3H_2O$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane).[15] The ΔE values are, respectively, 87 and 128 cm^{-1} for the two aforementioned triply bridged dimers. This comparison suggests that the ethoxo groups are less effective in transmitting the exchange interaction between the chromium(III) ions with respect to the hydroxo groups. These considerations may provide a starting point for a quantitative calculation of the exchange interaction in chromium(III) systems.

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