$(COOCH_3)^{2-}$ ligand, present in both the bridging and terminal modes of binding, is that one carboxylate function is essentially coplanar with the SC=CS frame while the other is approximately perpendicular to it. This structural feature is also observed in the structure of the $Mo(S_2C_2(COOCH_3)_2)_3^{2-}$ anion[1] and in the structures of complexes with the $S_2C{=}C(COOEt)_2^{2-}$ (DED) ligand.[38]

The intermetallic Fe–Fe distance in I is 3.120 (2) Å, considerably shorter than the corresponding distance in $Fe_2(EDT)_4^{2-}$ (II)[39] (3.410 (3) Å) but longer than its closer electronic and structural analogue $Fe_2(MNT)_4^{2-}$ (III) (3.083 (5) Å), Table V. Originally the difference between the Fe–Fe distances in II and III was interpreted[22] in terms of the considerable electron-withdrawing ability, or π-acidity differences between the MNT and EDT ligand, with the former being a much stronger π acid. The obvious difference of the same distances in I and III could very well reflect analogous π-acidity differences between the DMA and MNT ligands. This observation is consistent with the greater electron-withdrawing ability of CN vs. $COOCH_3$.

Acknowledgment. We are grateful to the Iowa Graduate College for providing the computing facilities and the National Science Foundation for a grant to purchase the X-ray crystallographic equipment. We also thank Prof. H. M. Goff for his assistance with the EPR spectra.

Registry No. I, 88358-02-5; $(Ph_4P)_2Fe_2S_{12}$, 71072-87-2; DMA, 762-42-5; Zn, 7440-66-6; S_8, 10544-50-0.

Supplementary Material Available: Listings of thermal parameters of non-hydrogen atoms, least-squares planes, positional and thermal parameters, and observed and calculated structure factors, and a stereoscopic view of the unit cell (Figure 5) (21 pages). Ordering information is given on any current masthead page.

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Contribution from the Dipartimento di Chimica,
Università di Firenze, 50132 Firenze, Italy

Crystal and Molecular Structure of a Dinuclear Chromium(III) Complex with a Linear Oxygen Bridge

MASSIMO DI VAIRA* and FABRIZIO MANI

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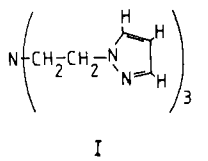
The dinuclear oxo-bridged chromium(III) complex $[\{Cr(NCS)(TPyEA)\}_2O](BPh_4)_2$, where TPyEA is the tetradentate ligand tris(2-pyrazol-1-ylethyl)amine, is formed by oxidation in CH_3CN or $(CH_3)_2CO$ solution of the chromium(II) complex $[Cr(NCS)(TPyEA)]BPh_4$. Crystal data for $[\{Cr(NCS)(TPyEA)\}_2O](BPh_4)_2$: triclinic, $P\bar{1}$, $Z = 2$, $a = 19.098$ (7) Å, $b = 14.688$ (5) Å, $c = 13.826$ (5) Å, $\alpha = 105.83$ (6)°, $\beta = 86.85$ (5)°, $\gamma = 101.78$ (6)°; $R = 0.077$ for 3361 reflections. Each of the metal atoms in the compound is in a distorted-octahedral environment formed by four nitrogen atoms of a TPyEA ligand, by the NCS nitrogen atom, and by the bridging oxygen atom. The Cr–O–Cr bridge is almost linear (Cr–O–Cr = 176.5 (6)°) and symmetrical with a 1.815 (6) Å mean value of the Cr–O distances. The value of μ_{eff} per Cr atom is 1.63 μ_B at 300 K and 0.98 μ_B at 86 K.

Although transition-metal systems containing two metal atoms linked by one bridging atom have been extensively investigated, only one μ-oxo complex of chromium(III) has been characterized so far in the solid state, namely the (μ-oxo)bis(pentaamminechromium(III)) chloride monohydrate, also known as the "basic rhodo" complex.[1,2]

We have found that the chromium(II) complex $[Cr(NCS)(TPyEA)]BPh_4$ formed by the tetradentate ligand tris(2-pyrazol-1-ylethyl)amine, TPyEA (I), undergoes rapid oxidation in solution, yielding the (μ-oxo)dichromium(III) complex with the formula $[\{Cr(NCS)(TPyEA)\}_2O](BPh_4)_2$, which has been isolated in the solid state. The structure of the latter complex, determined by X-ray diffraction methods, is reported here, and the spectral and magnetic properties of the compound are briefly discussed.



I

Experimental Section

Materials. All reagents and solvents used were of reagent grade purity. All operations on both the chromium(II) and the ^{18}O-labeled (μ-oxo)dichromium(III) complex were carried out in a nitrogen atmosphere with solvents deareated before their use. Oxygen-18 was purchased from Prochem (London); a sample containing 70% $^{18}O_2$ was employed. The syntheses of the ligand TPyEA and of the anhydrous chromium(II) halides have been reported in previous papers.[3,4]

Synthesis of $[Cr(NCS)(TPyEA)]BPh_4$. The ligand (10^{-3} mol) dissolved in 15 mL of ethanol was added to a warm solution of $Cr(NCS)_2$ (10^{-3} mol) in ethanol (25 mL), prepared in situ by the metathetic reaction of $CrBr_2(C_2H_5OH)_n$ and KNCS dissolved in ethanol. An excess of $NaBPh_4$ dissolved in 10 mL of boiling ethanol was added to the reactant solution. Crystallization of a blue compound occurred in a short time. The mother liquor was then eliminated by decantation, and the crystalline compound was washed several times by decantation with ethanol and diethyl ether. Finally, the compound was filtered off and dried in a stream of dry nitrogen at 80 °C. Anal. Calcd for $C_{40}H_{41}N_8CrBS$: C, 65.93; H, 5.67; N, 15.38. Found: C, 65.4; H, 5.55; N, 15.5.

Synthesis of $[\{Cr(NCS)(TPyEA)\}_2O](BPh_4)_2$. The blue $[Cr(NCS)(TPyEA)]BPh_4$ complex dissolved in acetone or acetonitrile is oxidized almost instantaneously by atmospheric O_2, giving a green solution from which a crystalline green compound with formula

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Table I. Summary of Crystal Data and Intensity Collection

formula	$C_{80}H_{82}B_2Cr_2N_{16}OS_2$
fw	1473.39
cryst system, space group	triclinic, $P\bar{1}$
a, Å	19.098 (7)
b, Å	14.688 (5)
c, Å	13.826 (5)
α, deg	105.83 (6)
β, deg	86.85 (5)
γ, deg	101.78 (6)
V, Å^3	3652.7
Z	2
D_{calcd}, g cm^{-3}	1.339
μ(Mo Kα), cm^{-1}	4.00
radiation	graphite-monochromated Mo Kα ($\lambda = 0.71069$ Å)
scan type	ω-2θ
scan speed, deg min^{-1}	5
scan width ($\Delta\omega$), deg	1.00 + 0.30 tan θ
bkgd	stationary counter-stationary crystal; symmetric at each end of scan
collection range	$\pm h, \pm k, +l$ ($2\theta \leq 40°$)
no. of unique data	6277
no. of data, $I > 3\sigma(I)$	3361
no. of variables	429
R^a	0.077
$R_w{}^a$	0.076
largest shift/error ratio^b	0.03

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. [b] Largest shift/error ratio in final least-squares cycle.

[{Cr(NCS)(TPyEA)}$_2$O](BPh$_4$)$_2$ is obtained in a nearly quantitative yield by concentrating to a small volume. The same green compound is obtained in smaller yield when the [Cr(NCS)(TPyEA)]BPh$_4$ complex is dissolved in deaerated CH_3CN or $(CH_3)_2CO$. In this case trace impurities of O_2, which may be present in spite of the effort to eliminate them, are presumably responsible for the oxidation of the chromium(II) complex. Anal. Calcd for $C_{80}H_{82}N_{16}Cr_2B_2OS_2$: C, 65.21; H, 5.61; N, 15.21; Cr, 7.06; O, 1.09; S, 4.36. Found: C, 65.4; H, 5.88; N, 15.0; Cr, 6.67; O, 1.86; S, 4.21.

The [{Cr(NCS)(TPyEA)}$_2{}^{18}$O](BPh$_4$)$_2$ complex was prepared by dissolving [Cr(NCS)(TPyEA)]BPh$_4$ in acetone saturated with oxygen-18 (70% enriched). The solution was then concentrated by boiling under a nitrogen atmosphere until crystallization occurred.

The [Cr(NCS)(TPyEA)]BPh$_4$ complex is stable in the solid state under inert atmosphere but rapidly oxidizes in air, yielding a brown material that does not contain oxo bridges.

Physical Measurements. Magnetic and spectrophotometric measurements on the complexes were performed with the apparatus already described on samples contained in suitable airtight containers (Gouy tube, UV cells) filled in a drybox under an inert atmosphere.[5] The absorption spectrum of the (μ-oxo)dichromium(III) complex was carried out with a Cary 17D spectrophotometer in an acetonitrile solution at ca. 10^{-4} mol dm^{-3} concentration.

Significant vibrational frequencies for the complexes are as follows. [Cr(NCS)(TPyEA)]BPh$_4$: ν(CN) 2085 s, br cm^{-1}. [{Cr(NCS)(TPyEA)}$_2$O](BPh$_4$)$_2$: ν(CN) 2060 s cm^{-1}, ν(Cr–^{16}O–Cr) 830 s cm^{-1}, ν(Cr–^{18}O–Cr) 790 s cm^{-1}. (s = strong; br = broad.)

UV–visible spectrum of [{Cr(NCS)(TPyEA)}$_2$O](BPh$_4$)$_2$ (CH_3CN): 655 nm (ϵ 70), 575 (51), 490 (90), 427 (480), 365 (1530), 336 (11 200), 273 (6670), 268 (6860).

Collection and Reduction of X-ray Data. A crystal of the compound [{Cr(NCS)(TPyEA)}$_2$O](BPh$_4$)$_2$ shaped as a flat parallelepiped with dimensions 0.10 × 0.25 × 0.27 mm was used for crystal data and intensity data collections. A Philips PW 1100 automated diffractometer was used for all operations. Lattice constants were determined at 22 °C from the setting angles of 24 reflections with $11° < \theta < 16°$. Details of crystal data and data collection are listed in Table I. The variation in intensity of three standard reflections measured every 120 min was less than 2%. The data were corrected for Lorentz and polarization effects. No correction for absorption was necessary in view of the small value of μ and of the small variations in transmitted intensities during ψ scans. The principal computer programs used in the crystallographic calculations are listed in ref 6.

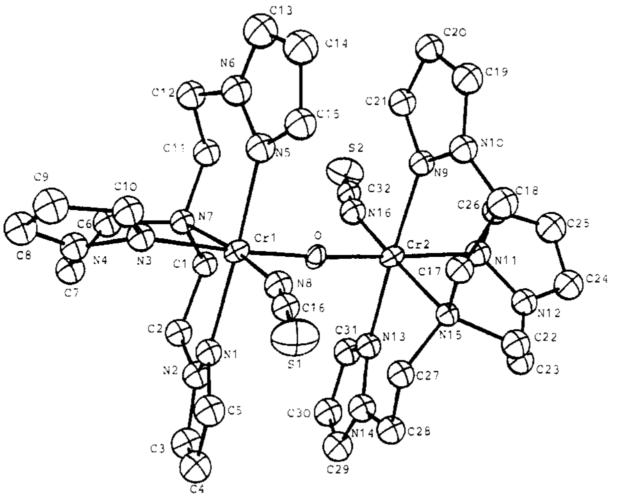

Figure 1. Perspective view of the [{Cr(NCS)(TPyEA)}$_2$O]$^{2+}$ cation with 30% probability ellipsoids.

Solution and Refinement of the Structure. The positions of the metal atoms were determined from a Patterson map, and those of all the other non-hydrogen atoms were located in subsequent Fourier maps. Full-matrix least-squares refinement was based on minimization of the function $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(F_o)$. Anisotropic thermal parameters were used for the Cr, S, and O atoms whereas isotropic thermal parameters were applied to the N, C, and B atoms. A phenyl group of a BPh$_4$ anion was found to be disordered between two orientations whose occupancy factors were refined. The two fractions of the ring were refined as rigid groups with temperature factors of the carbon atoms linked to an overall value but constrained to increase with the distance from the boron atom. Hydrogen atoms were introduced in calculated positions (C–H = 1.00 Å) as fixed contributions, each with a temperature factor ca. 20% larger than that of the respective carbon atom. The scattering factors for the neutral atoms were taken from ref 7 and the anomalous dispersion correction terms for Cr from ref 8. The final R values are reported in Table I. The highest peaks in the final difference map (<0.7 e Å^{-3}) were located in the region of the disordered phenyl group. The final positional parameters for the non-hydrogen atoms are given in Table II. Listings of thermal parameters for the non-hydrogen atoms, hydrogen atom coordinates, and the observed and calculated structure amplitudes are available as supplementary material.

Results and Discussion

From the reaction of $Cr(NCS)_2$ and the ligand TPyEA in ethanol under anaerobic conditions, the chromium(II) complex with formula [Cr(NCS)(TPyEA)]BPh$_4$ has been obtained ($\mu_{\text{eff}} = 4.74\ \mu_B$ (295 K), 4.42 μ_B (86 K)). This compound is extremely sensitive to oxidation both in the solid state and in solution. It oxidizes almost instantaneously when dissolved in CH_3CN or $(CH_3)_2CO$ (see Experimental Section), yielding a green crystalline compound that was assigned the formula [{Cr(NCS)(TPyEA)}$_2$O](BPh$_4$)$_2$. The latter compound is quite stable both in the solid state and in CH_3CN or $(CH_3)_2CO$ solution. It exhibits a feeble paramagnetism corresponding to a μ_{eff} value of 1.63 μ_B/Cr atom at 300 K, which decreases with decreasing temperature, reaching a value of 0.98 μ_B at 86 K. An X-ray diffraction study was undertaken on this compound in order to determine its structure and

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(8) Reference 7, p 148 ff.

Table II. Positional Parameters for the Structure of $[\{Cr(NCS)(TPyEA)\}_2O](BPh_4)_2$[a,b]

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Cr1	2741 (1)	1833 (1)	3515 (1)	C35	9213 (4)	1404 (5)	4612 (5)
Cr2	2174 (1)	3135 (1)	5959 (1)	C36	8957 (4)	2101 (5)	5327 (5)
S1	4917 (2)	3722 (3)	2823 (3)	C37	8507 (4)	2607 (5)	5037 (5)
S2	151 (2)	1181 (3)	6931 (3)	C38	8343 (4)	2413 (5)	4026 (5)
O	2443 (3)	2505 (4)	4721 (4)	C39	8561 (4)	504 (5)	1425 (5)
N1	2218 (4)	2497 (4)	2698 (4)	C40	9234 (4)	263 (5)	1134 (5)
N2	1498 (4)	2445 (4)	2645 (5)	C41	9301 (5)	−692 (5)	663 (5)
N3	3124 (4)	996 (4)	2158 (4)	C42	8717 (5)	−1401 (5)	466 (5)
N4	2707 (4)	394 (4)	1363 (4)	C43	8042 (5)	−1225 (5)	719 (5)
N5	3327 (4)	1150 (5)	4237 (5)	C44	7975 (4)	−255 (5)	1207 (5)
N6	3095 (4)	262 (5)	4397 (5)	C45	7662 (4)	1771 (5)	1886 (5)
N7	1799 (4)	731 (4)	3325 (4)	C46	7075 (4)	1419 (5)	2410 (5)
N8	3642 (4)	2793 (4)	3477 (4)	C47	6395 (5)	1548 (5)	2242 (5)
N9	2836 (4)	2557 (4)	6665 (4)	C48	6282 (5)	2010 (5)	1551 (5)
N10	3536 (4)	2961 (4)	6932 (5)	C49	6832 (5)	2366 (5)	1032 (5)
N11	1889 (4)	3856 (4)	7438 (4)	C50	7527 (4)	2245 (5)	1184 (5)
N12	1913 (4)	4846 (4)	7773 (5)	C51	9069 (4)	2444 (5)	1704 (5)
N13	1450 (4)	3739 (4)	5361 (4)	C52	9311 (4)	3354 (5)	2355 (5)
N14	1588 (4)	4365 (4)	4777 (5)	C53	9750 (4)	4099 (5)	2040 (5)
N15	2950 (4)	4412 (4)	5942 (4)	C54	9975 (4)	3956 (5)	1056 (5)
N16	1368 (4)	2065 (4)	6123 (4)	C55	9783 (5)	3087 (5)	418 (5)
C1	1162 (4)	1211 (5)	3618 (5)	C56	9330 (4)	2326 (5)	718 (5)
C2	944 (4)	1668 (5)	2858 (5)	C57	7231 (4)	3166 (5)	8024 (5)
C3	1359 (5)	3049 (5)	2108 (5)	C58	7430 (4)	2518 (5)	8474 (5)
C4	1992 (5)	3514 (5)	1877 (5)	C59	8148 (5)	2493 (5)	8588 (5)
C5	2533 (4)	3173 (5)	2221 (5)	C60	8686 (5)	3082 (5)	8266 (5)
C6	1627 (4)	4 (5)	2314 (5)	C61	8523 (5)	3770 (5)	7822 (5)
C7	1936 (4)	313 (5)	1415 (5)	C62	7800 (4)	3774 (5)	7721 (5)
C8	3125 (5)	−60 (5)	658 (5)	C63	5818 (4)	2449 (5)	8210 (5)
C9	3796 (5)	216 (5)	954 (5)	C64	5473 (4)	2529 (5)	9137 (5)
C10	3791 (4)	876 (5)	1896 (5)	C65	4961 (5)	1794 (5)	9331 (5)
C11	1820 (4)	186 (5)	4120 (5)	C66	4755 (5)	950 (5)	8636 (5)
C12	2432 (4)	−346 (5)	4020 (5)	C67	5081 (5)	805 (5)	7709 (5)
C13	3635 (5)	46 (5)	4847 (5)	C68	5600 (5)	1547 (5)	7518 (5)
C14	4171 (5)	754 (5)	5002 (5)	C69	6266 (4)	3272 (5)	6770 (5)
C15	3983 (4)	1460 (5)	4601 (5)	C70	5762 (4)	3714 (5)	6477 (5)
C16	4188 (4)	3194 (5)	3204 (5)	C71	5567 (5)	3540 (5)	5474 (5)
C17	3678 (4)	4193 (5)	5992 (5)	C72	5891 (4)	2972 (5)	4711 (5)
C18	3848 (4)	3934 (5)	6927 (5)	C73	6438 (5)	2588 (5)	4953 (5)
C19	3816 (4)	2343 (5)	7303 (5)	C74	6622 (4)	2751 (5)	5967 (5)
C20	3329 (4)	1547 (5)	7278 (5)	C751	6373 (3)	4405 (5)	8771 (5)
C21	2723 (4)	1695 (5)	6873 (5)	C761	6851 (3)	4790 (5)	9575 (5)
C22	2926 (4)	5338 (5)	6734 (5)	C771	6813 (3)	5680 (5)	10247 (5)
C23	2189 (4)	5470 (5)	7136 (5)	C781	6298 (3)	6186 (5)	10114 (5)
C24	1694 (5)	5070 (5)	8748 (5)	C791	5820 (3)	5801 (5)	9309 (5)
C25	1503 (5)	4238 (5)	9033 (5)	C801	5858 (3)	4910 (5)	8638 (5)
C26	1620 (4)	3508 (5)	8197 (5)	C752	6215 (3)	4327 (6)	8796 (6)
C27	2915 (4)	4573 (5)	4916 (5)	C762	6789 (3)	4927 (6)	9382 (6)
C28	2294 (4)	4967 (5)	4720 (5)	C772	6690 (3)	5776 (6)	10083 (6)
C29	966 (5)	4451 (5)	4431 (5)	C782	6017 (3)	6025 (6)	10199 (6)
C30	414 (5)	3892 (5)	4760 (5)	C792	5444 (3)	5425 (6)	9613 (6)
C31	736 (4)	3466 (5)	5346 (5)	C802	5543 (3)	4576 (6)	8912 (6)
C32	856 (4)	1674 (5)	6463 (5)	B1	8475 (5)	1588 (5)	2053 (5)
C33	8613 (4)	1730 (5)	3251 (5)	B2	6411 (5)	3323 (5)	7935 (5)
C34	9036 (4)	1212 (5)	3604 (5)				

[a] Multiplied by 10^4. Estimated standard deviations on the last significant digit are in parentheses. [b] Atoms C33–C56 and C57–C802, respectively, belong to the phenyl groups of the two BPh_4 anions. Atoms C751–C801 and C752–C802 form the two fractions of the disordered phenyl group, having 0.70 and 0.30 population parameters.

possibly rationalize its properties.

The structure of the compound $[\{Cr(NCS)(TPyEA)\}_2O](BPh_4)_2$ consists of dinuclear $[\{Cr(NCS)(TPyEA)\}_2O]^{2+}$ cations and of BPh_4^- anions. Each of the metal atoms in the cation (Figure 1) is in a distorted-octahedral environment formed by the four nitrogen donor atoms of the TPyEA ligand, by the NCS nitrogen atom, and by the bridging oxygen atom. Selected values of bond distances and angles in the cation are reported in Table III. The tetradentate ligands, each spanning two faces of the octahedron about the respective metal atom, lie in trans positions with respect to each other, so that the inner skeleton of the complex approaches D_{4h} effective symmetry with N–Cr–Cr–N dihedral angles, formed by the four pairs of N atoms in essentially eclipsed positions, ranging from 5.3 to 13.1°. The Cr–O–Cr bridge is essentially linear (Cr–O–Cr = 176.5 (6)°) with the mean value of the Cr–O distances (1.815 (6) Å) close to that of 1.821 (3) Å found for the $[(NH_3)_5CrOCr(NH_3)_5]^{4+}$ cation.[2] The two Cr–N bonds lying trans to the oxygen atom position (Cr1–N3 = 2.13 (1) Å, Cr2–N11 = 2.13 (1) Å) are significantly longer than the other four Cr–N bonds formed by pyrazole nitrogens, which average to 2.088 (12) Å.

The spectral and magnetic properties of the present dinuclear compound differ from those generally exhibited by chromium(III) complexes whereas they are similar to the properties of salts of the $[(NH_3)_5CrOCr(NH_3)_5]^{4+}$ "basic rhodo" cation.[1,2,9–12] A band at 830 cm^{-1} in the IR spectrum

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Table III. Selected Bond Lengths (Å) and Angles (deg) for the Structure of $[\{Cr(NCS)(TPyEA)\}_2O](BPh_4)_2$

Cr1-O	1.82 (1)	Cr2-O	1.81 (1)
Cr1-N1	2.08 (1)	Cr2-N9	2.07 (1)
Cr1-N3	2.13 (1)	Cr2-N11	2.13 (1)
Cr1-N5	2.09 (1)	Cr2-N13	2.10 (1)
Cr1-N7	2.13 (1)	Cr2-N15	2.14 (1)
Cr1-N8	2.00 (1)	Cr2-N16	2.02 (1)
Cr1-O-Cr2	176.5 (6)	O-Cr2-N9	92.3 (4)
O-Cr1-N1	93.5 (4)	O-Cr2-N11	177.8 (4)
O-Cr1-N3	176.1 (4)	O-Cr2-N13	92.4 (4)
O-Cr1-N5	90.7 (4)	O-Cr2-N15	91.8 (3)
O-Cr1-N7	92.8 (3)	O-Cr2-N16	95.9 (3)
O-Cr1-N8	95.1 (3)	N9-Cr2-N11	85.5 (4)
N1-Cr1-N3	90.4 (4)	N9-Cr2-N13	174.9 (4)
N1-Cr1-N5	175.2 (4)	N9-Cr2-N15	95.1 (4)
N1-Cr1-N7	86.9 (4)	N9-Cr2-N16	87.9 (4)
N1-Cr1-N8	89.9 (4)	N11-Cr2-N13	89.8 (4)
N3-Cr1-N5	85.4 (4)	N11-Cr2-N15	88.1 (3)
N3-Cr1-N7	87.3 (3)	N11-Cr2-N16	84.3 (4)
N3-Cr1-N8	85.0 (4)	N13-Cr2-N15	86.7 (4)
N5-Cr1-N7	95.1 (4)	N13-Cr2-N16	89.7 (4)
N5-Cr1-N8	87.5 (4)	N15-Cr2-N16	171.6 (4)
N7-Cr1-N8	171.6 (4)	Cr2-N16-C32	159.0 (8)
Cr1-N8-C16	162.1 (8)		

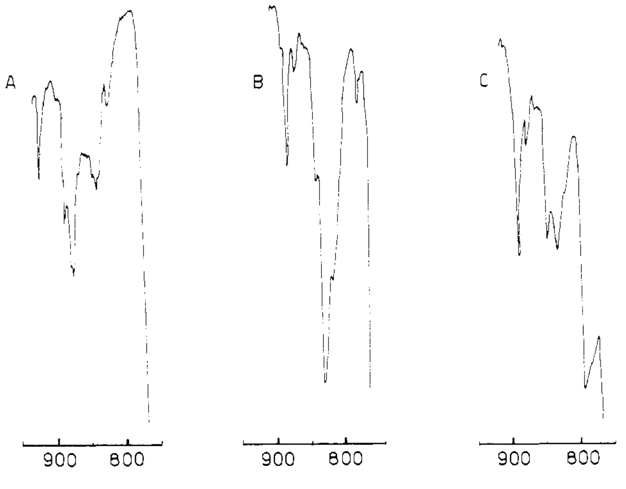

Figure 2. IR spectra (Nujol) in the 750–950-cm^{-1} region: A, $[Cr(NCS)(TPyEA)]BPh_4$; B, $[\{Cr(NCS)(TPyEA)\}_2{}^{16}O](BPh_4)_2$; C, $[\{Cr(NCS)(TPyEA)\}_2{}^{18}O](BPh_4)_2$.

of the former compound, which is not present in that of the parent $[Cr(NCS)(TPyEA)]BPh_4$ complex, is assigned to the asymmetric Cr–O–Cr stretch.[13] Its intensity decreases whereas a new band appears at 790 cm^{-1} in the spectra of ^{18}O-enriched samples (Figure 2). In the 300–450-nm region of the electronic spectrum of the dinuclear complex (Figure

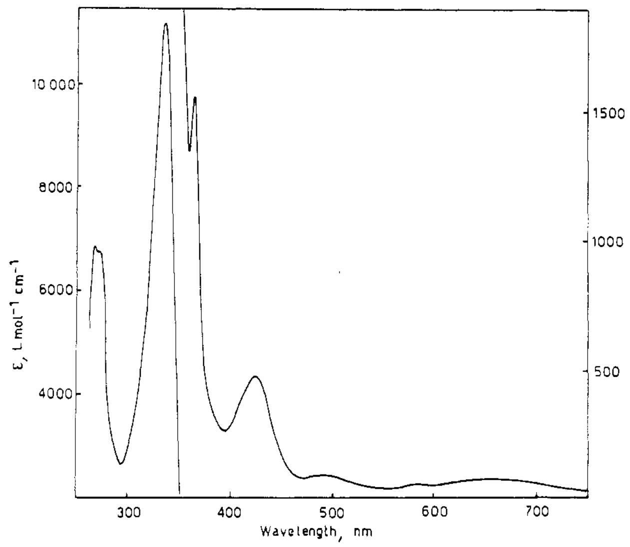

Figure 3. Electronic spectrum of $[\{Cr(NCS)(TPyEA)\}_2O](BPh_4)_2$ in CH_3CN solution.

3), at least three rather sharp and intense bands are observed that are not present in the spectrum of the $[Cr(NCS)(TPyEA)]BPh_4$ complex nor in those of chromium(III) complexes formed by similar ligands.[14]

The magnetic moment (see above) of the present dinuclear compound, which is much lower than expected for a chromium(III) derivative, as well as its temperature dependence is indicative of a strong antiferromagnetic coupling occurring through the oxygen bridge. This is in line with the existence of a short, essentially linear, oxygen bridge and with the approximate D_{4h} symmetry of the inner skeleton of the cation, which allows maximum π interactions within the Cr–O–Cr fragment.

A rationalization of the main spectral and magnetic properties of the present dinuclear compound may be provided by the approaches already used for the isoelectronic "basic rhodo" complex[9–12] and for other complexes with a structure of their inner skeleton similar to that of $[\{Cr(NCS)(TPyEA)\}_2O](BPh_4)_2$.[15,16]

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Registry No. $[Cr(NCS)(TPyEA)]BPh_4$, 88130-41-0; $[\{Cr(NCS)(TPyEA)\}_2O](BPh_4)_2$, 88130-43-2; ^{18}O, 14797-71-8.

Supplementary Material Available: Listings of thermal parameters for non-hydrogen atoms (Table SI), hydrogen atom coordinates (Table SII), bond distances (Table SIII), bond angles (Table SIV), and observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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