N(8), O(4), and O(16) and intramolecular repulsion between O(4) and O(16) [O(4)···O(16) = 2.94 (2)–3.04 (2) Å for individual [LH$_3$]$^+$ ions]. On the other hand, the bond lengths and angles in the pyrimidine and phenyl moieties compare reasonably well with those reported for other complexes of analogous ligands.[2,8,9,11,43]

As stated earlier, the hydrogen atoms could not be found from the difference Fourier map due to the modest quality of the single crystal. Yet, the observed intermolecular contact distances (supplementary Table VIII) suggest a hydrogen-bond network between the cations, anions, and solvent molecules. There are short contact distances between the amino nitrogen of each [LH$_3$]$^+$ cation and two bromine atoms. Also the geometry supports the assumption that both hydrogen atoms of each amino group participate in hydrogen-bond formation between the atoms (Figure 2). Moreover, three bromine atoms, Br(3), Br(7), and Br(2), seem to form hydrogen bonds with the oxygen atoms of the crystal water molecule, O(503), the methanol molecule, O(501), and the methanol molecule, O(504b), respectively. Thus each bromine atom could participate in one or two hydrogen bonds. The oxygen atoms of the three independent methanol molecules and the crystal water molecule participate in fairly strong hydrogen bonds [O···O

= 2.55 (4)–2.65 (3) Å], if only the oxygen–oxygen distances are considered. The assumed hydrogen bonds formed by the solvent molecules probably contribute to the stability of the crystals.

Supplementary Material Available: Tables listing the X-ray diffraction measurement details and complete crystal data (Table SI), atomic coordinates for the four cations, hydrogen atom parameters, and anisotropic thermal parameters for the copper and bromine atoms (Table SII), selected bond lengths and angles for the cations (Table IV), ideal and observed dihedral angles for the [CuBr$_4$]$^{2-}$ polyhedra (Table V), least-squares mean planes (Table VII), and selected intermolecular contacts (Table VIII) (20 pages); a table of calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Spectral and Magnetic Properties of (μ-Carbonato)(μ-hydroxo)-bis[N,N'-(bis(2-aminoethyl)ethane-1,2-diamine)chromium(III)] Perchlorate

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The μ-carbonato μ-hydroxo complex [(tren)Cr(μ-CO$_3$)(μ-OH)Cr(tren)](ClO$_4$)$_3$·2H$_2$O has been prepared from both Cr(II) and Cr(III) precursors and characterized by structural analysis, magnetic susceptibility measurements, and luminescence spectroscopy. The complex crystallizes in the monoclinic space group P2$_1$/c (No. 14) with a = 7.022 (1) Å, b = 25.679 (8) Å, c = 8.646 (2) Å, β = 102.27 (2)°, V = 1523.4 (7) Å^3, and Z = 2. Least-squares refinement led to final R and R_w values of 0.054 and 0.043, respectively, for 1857 observed reflections with $F \geq 6\sigma(F)$. In the complex cation, the two Cr(III) centers are in a distorted octahedral environment and are linked by a carbonate and a hydroxide bridge. Within the bridging moiety, Cr–O(CO$_3$) = 1.954 (4) Å, Cr–O(OH) = 1.944 (2) Å, Cr–OH–Cr = 131.5 (3)°, and O–Cr–O = 94.5 (2)°, while the Cr–N distances are 2.081 (4) Å. Magnetic susceptibility measurements in the temperature range 4.2–300 K indicate that the Cr centers are weakly antiferromagnetically coupled (J = −16.8 cm^{-1}). The luminescence spectrum of the complex at 1.5 K showed four transitions from the luminescent lowest excited state (S^* = 2) to the ground state (S = 0, 1, 2, 3), and from the splitting pattern, a J value of −18.5 (±0.1) cm^{-1} was determined, consistent with the susceptibility data. The degree of coupling between the metal centers is similar to that observed in related complexes containing hydroxo bridges. A correlation between coupling constant and the average of the shortest Cr–O distance in binuclear Cr(III) complexes similar to that reported for Fe(III) complexes cannot be developed at this stage because of an insufficient number of oxo-bridged complexes with short Cr–O distances.

Introduction

Polynuclear metal complexes are attracting attention not only because of the important functions polynuclear sites perform in biological systems[1] but also because of fundamental interest in understanding the magnetic and spectroscopic properties of these complexes.[2] Numerous complexes are now known in which the metal centers are linked by acetate, oxo, and hydroxo bridging groups,[3] and a clearer picture of the factors affecting M···M interactions is emerging.[2] Correlations between magnetic properties and structural parameters have been developed for Cu(II), Fe(III), and hydroxo-bridged Cr(III) complexes.[2,4] The most recent of these, reported by Gorun and Lippard,[4] suggests that the coupling constants for most doubly and triply bridged Fe(III) complexes follow a relatively simple dependence on the average

of shortest metal to bridging group distances.

Comparatively few complexes containing carbonato bridging groups have been structurally characterized, and apart from some Fe(III)[5–7] and Cu(II)[8] complexes, the effect of carbonato bridges

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on M···M communication has been little explored. For Fe(III) complexes, weaker antiferromagnetic coupling is found in μ-oxo μ-carbonato complexes than in the μ-oxo-μ-acetato analogues. For example, $J = -91$ cm^{-1} for [(Me₃tacn)Fe(μ-O)(μ-CO₃)₂Fe(Me₃tacn)]·4.2H₂O is smaller than $J = -119$ cm^{-1} observed for [(Me₃tacn)Fe(μ-O)(μ-CO₂CH₃)₂Fe(Me₃tacn)](ClO₄)₂·H₂O (Me₃tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane),[9] while that for [(tmpa)Fe(μ-O)(μ-CO₃)Fe tmpa](ClO₄)₂ ($J = -108$ cm^{-1}) is only slightly smaller than $J = -114$ cm^{-1} for [(tmpa)Fe(μ-O)(μ-CO₂CH₃)Fe(tmpa)](ClO₄)₃ (tmpa = tris(2-pyridylmethyl)amine).[7] These variations in magnetic properties can be rationalized in terms of the model proposed by Gorun and Lippard.[4] In the case of Cr(III), few carbonato-bridged complexes are known. Bang et al.[10] have recently reported the structure and magnetic properties of a singly bridged carbonato complex, *trans*-[(NH₃)(cyclam)Cr(μ-CO₃)Cr(cyclam)(NH₃)]I₄·2H₂O (cyclam = 1,4,8,11-tetraazacyclotetradecane), in which the Cr(III) centers show weak antiferromagnetic coupling ($J = -2.6$ cm^{-1}). The structure of [(tacn)Cr(μ-OH)₂(μ-CO₃)Cr(tacn)]I₂·2H₂O (tacn = 1,4,7-triazacyclononane) is known,[11] but no measurements of magnetic and spectroscopic properties are available at present. The effect of carbonato bridges on Cr···Cr interactions is further analyzed in this paper.

Concerns about the increasing levels of CO₂ in the atmosphere are contributing to the growing importance of carbonato complexes in general. There is, of course, much information available on the activation of CO₂ by transition metal complexes, aimed at the catalytic conversion of CO₂ into organic compounds.[12-14] Fixation of CO₂ by metal complexes in the form of either CO₃²⁻ or HCO₃⁻ is being examined as an alternative solution,[13-15] but most metal complexes are not sufficiently reactive to form carbonato complexes under atmospheric conditions.[15] Two exceptions are the complexes [LCu(μ-OH)₂CuL], where L = hydrotris(3,5-diisopropylpyrazol-1-ylborate, and [(tacn)(H₂O)Rh(μ-OH)₂Rh(H₂O)(tacn)]⁴⁺, which, under appropriate conditions, react with atmospheric CO₂ to produce [LCu(μ-CO₃)CuL][15] and [(tacn)Rh(μ-CO₃)(μ-OH)₂Rh(tacn)](ClO₄)₂·3H₂O,[11] respectively. The cyclam complex *trans*-[(NH₃)(cyclam)Cr(μ-CO₃)Cr(cyclam)(NH₃)]I₄·2H₂O was obtained as a side product in the preparation of [Cr(cyclam)(NH₃)₂]³⁺ from a mixture of *cis*- and *trans*-[Cr(cyclam)Cl₂]⁺.[10]

We report here the synthesis, crystal structure, magnetic properties, and luminescence spectra of the binuclear complex [(tren)Cr(μ-CO₃)(μ-OH)Cr(tren)](ClO₄)₃·2H₂O (tren = N,N′-bis(2-aminoethyl)ethane-1,2-diamine). The complex was initially isolated from solutions of [(tren)Cr(OH₂)₂]³⁺ which had been left in contact with air at elevated temperatures and therefore provides another example of CO₂ fixation under atmospheric conditions.

Experimental Section

Compound Preparation. [(tren)CrCl₂]Cl[16] and solutions of [Cr(OH₂)₆](ClO₄)₂[17] were prepared by literature methods. Silver perchlorate

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Table I. Crystal Data for [(tren)Cr(μ-OH)(μ-CO₃)Cr(tren)](ClO₄)₃·2H₂O

chem formula	C₁₃Cl₃H₄₁N₈O₁₈Cr₂	Z	2
fw	807.9	T, °C	20 (1)
space group	P2₁/c (No. 14)	ρ, g cm^{-3}	1.74 (2)
a, Å	7.022 (1)^a	μ(Mo Kα), cm^{-1}	10.5
b, Å	25.679 (8)^a	λ, Å	0.710 73
c, Å	8.646 (2)^a	$R(F_o)^b$	0.054
β, deg	102.27 (2)^a	$R_w(F_o)^c$	0.043
V, Å³	1523.4 (7)		

^{a}Cell parameters were derived by least-squares calculations from angular settings of 25 reflections measured in the range $5° < 2\theta < 21°$. $^b R(F_o) = (\sum(|F_o| - |F_c|)^2/\sum|F_o|^2)^{1/2}$. $^c R_w(F_o) = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ where $w = (\sigma^2(F_o))^{-1}$.

solutions were prepared either from silver perchlorate or by dissolving silver(I) oxide in stoichiometric quantities of perchloric acid. All other reagents were of laboratory grade or better and were used as received.

Caution! Although no problems have been encountered in this work, perchlorate salts are potentially explosive and care should be exercised when heating or grinding these salts.

Synthesis of [(tren)Cr(μ-CO₃)(μ-OH)Cr(tren)](ClO₄)₃·2H₂O. Method A. [(tren)CrCl₂]Cl (0.5 g, 1.6 mmol) was dissolved in 25 mL of H₂O, and silver perchlorate (1.0 g, 4.8 mmol) was added. A few drops of sodium hydroxide solution were added to adjust the suspension pH to about 9. The mixture was then heated on a steam bath for about 5 h to ensure complete precipitation of chloride as silver chloride. The suspension was cooled to room temperature and filtered to remove the precipitate. The filtrate was evaporated to dryness under vacuum. The residue was dissolved in a minimum amount of water (10–15 mL) with warming, and the solution was filtered to remove any suspended material. Purple-brown crystals were obtained after several days, which were collected by filtration, washed with ice-cold water, and dried in a desiccator. Yield: 0.13 g (20%).

Method B. [(tren)CrCl₂]Cl (0.5 g, 1.6 mmol) was dissolved in water (25 mL), and a solution of silver perchlorate (0.46 g of Ag₂O dissolved in HClO₄, final pH = 2) was added. After the mixture was heated on a steam bath for 1 h, silver chloride was removed by filtration. The pH of the purple supernatant was adjusted to about 8, and sodium bicarbonate (0.2 g, 2.4 mmol) was added. The solution turned brownish purple within minutes but was heated on a steam bath for a further 3 h while a volume of more than 10 mL was maintained. At this time, 2 g of sodium perchlorate was added, and the solution was allowed to stand at room temperature for several days to allow precipitation of the brown-purple crystalline product. Yield: 0.42 g (65%).

Method C. Tren (2 g, 1.6 mmol) was added slowly to a stirred solution of [Cr(OH₂)₆](ClO₄)₂ (11.5 mmol) at ambient temperature. A color change from the characteristic sky blue of Cr²⁺ to a dark blue was observed, indicating coordination of the ligand. To this solution was added a degassed solution of sodium bicarbonate (0.6 g, 7 mmol in 10 mL of H₂O). Air was then bubbled through the mixture for 30 min to allow oxidation of Cr(II) to Cr(III). The mixture was then filtered to remove any insoluble precipitate, evaporated to a small volume (15–20 mL), and cooled in a refrigerator. Purple-brown crystals formed, which were collected as described above. Yield: 2.3 g (50%).

Anal. Calcd for Cr₂C₁₃Cl₃H₄₁N₈O₁₈: C, 19.3; H, 5.1; N, 13.9; Cl, 13.2; Cr, 12.9. Found (product produced by method A): C, 19.4; H, 5.0; N, 13.7; Cl, 12.8; Cr, 12.6. The same Cr content was found for products produced by methods B and C. Solution UV–vis data [λ, nm (ε, M^{-1} cm^{-1})]: (a) 1 M HClO₄, 511 (270), 392 (142); (b) 1 M NaOH 725 sh (50), 690 sh (70), 599 (122), 508 sh (105), 445 (138), 360 (161). IR data (KBr): ν_CO 1493 (vs), 1376 (vs), 895 (m), 692 (m) cm^{-1}.

Crystal Structure Determination. Crystal data and refinement parameters are given in Table I. A representative brown-purple acicular crystal of approximate dimensions (0.22 × 0.15 × 0.08 mm) was used for data collection. Intensity measurements were made on a Nicolet R3m/V diffractometer using graphite-monochromated Mo Kα radiation with $3.5° < 2\theta < 50.0°$, operating in an ω-scan mode with a scan range of 1.3°, at a scan rate between 2.00 and 10.19° min^{-1}. A total of 2755 unique data were collected (+h,+k,±l), 1857 of which were considered to be observed ($F > 6\sigma(F)$). Three standard reflections monitored every 197 reflections showed no significant variation in intensity over the data collection period. Intensity data were corrected for Lorentz and polarization effects. A numerical absorption correction was applied,[18] the maximum and minimum transmission factors being 0.991 and 0.983,

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Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{Å}^2 \times 10^3$)

	x	y	z	$U(\text{eq})^a$
Cr	376 (1)	3190 (1)	3334 (1)	19 (1)
Cl(1)	5176 (3)	5503 (1)	2375 (2)	40 (1)
Cl(2)	3695 (4)	7500	2559 (3)	35 (1)
N(1)	−606 (7)	3957 (2)	3191 (5)	22 (1)
N(2)	−236 (7)	3256 (2)	879 (5)	27 (1)
N(3)	3090 (7)	3539 (2)	3516 (5)	25 (1)
N(4)	488 (7)	3294 (2)	5741 (5)	29 (1)
O(1)	3251 (8)	5304 (2)	1880 (6)	80 (2)
O(2)	6499 (9)	5133 (2)	3155 (7)	93 (3)
O(3)	5184 (8)	5941 (2)	3367 (7)	86 (2)
O(4)	5802 (9)	5682 (2)	1022 (6)	95 (3)
O(5)	3653 (9)	7500	883 (7)	50 (3)
O(6)	4470 (15)	7073 (3)	3273 (8)	176 (5)
O(7)	1755 (15)	7500	2713 (12)	145 (6)
C(1)	−1551 (8)	4034 (2)	4569 (6)	28 (1)
C(2)	−227 (9)	3821 (2)	6056 (7)	31 (2)
C(3)	−2036 (8)	4000 (2)	1659 (6)	28 (1)
C(4)	−1164 (9)	3769 (2)	342 (7)	33 (2)
C(5)	1096 (8)	4330 (2)	3280 (7)	30 (2)
C(6)	2841 (9)	4070 92)	2817 (7)	31 (2)
C(7)	−3224 (12)	2500	2953 (9)	21 (2)
O(8)	−5050 (9)	2500	2561 (6)	34 (1)
O(9)	−2284 (6)	2933 (1)	3134 (4)	31 (1)
O(10)	1533 (8)	2500	3439 (6)	25 (1)
O(11)	3266 (8)	3274 (2)	9577 (6)	90 (2)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.
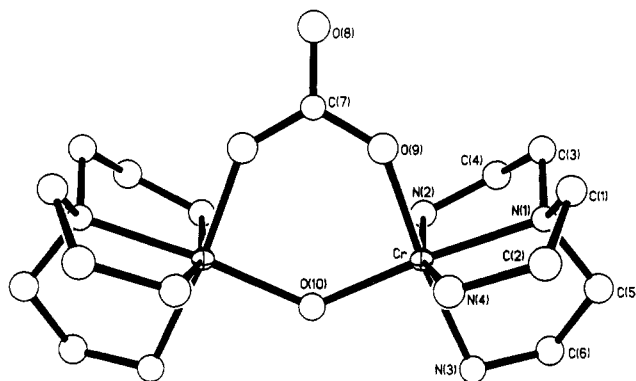
Figure 1. ORTEP drawing and atomic labeling scheme of the [(tren)Cr-(μ-OH)(μ-CO$_3$)Cr(tren)]$^{3+}$ cation with 50% thermal ellipsoids.

respectively. The atomic scattering factors for neutral atoms were taken from ref 19 and were corrected for anomalous dispersion by using values from ref 19. All calculations were performed on a MicroVAX 2000 computer. The program used for refinement was that due to Sheldrick.[18]

The structure was solved by direct methods. Full-matrix least-squares refinement employing anisotropic thermal parameters for Cr and for Cl and O from the perchlorate groups and isotropic thermal parameters for all other atoms (single variable isotropic thermal parameter for hydrogen which refined to 0.031 (4) Å^2—positioned in geometrically idealized positions: C–H = 0.96 Å), reduced R to 0.054 and R_w to 0.043 at convergence, where $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ and $w = (\sigma^2 - (F_o))^{-1}$. The goodness of fit value $(|\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2})$ was 2.74. The largest peak in the difference Fourier synthesis was 1.05 e Å^{-3}.

Final atomic parameters are given in Table II, bond lengths and angles are given in Table III, and Figure 1 shows the discrete dimeric pairs which exist in the structure and the atomic labeling scheme.

Physical Measurements. Average magnetic susceptibilities were measured on a powdered sample of the complex using an extensively modified Oxford Instruments magnetometer.[20] Measurements were carried out between 4.2 and 300 K with a main field of 10 kG and a gradient of 1 kG/cm. In the temperature range 4.2–20 K, the data were obtained manually, while at higher temperatures, direct computer ac-

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Table III. Bond Lengths (Å) and Angles (deg) in 1

Cr–N(1)	2.081 (4)	Cr–N(2)	2.081 (4)
Cr–N(3)	2.081 (5)	Cr–N(4)	2.083 (4)
Cr–O(9)	1.954 (4)	Cr–O(10)	1.944 (2)
Cl(1)–O(1)	1.423 (5)	Cl(1)–O(2)	1.398 (5)
Cl(1)–O(3)	1.414 (6)	Cl(1)–O(4)	1.411 (6)
Cl(2)–O(5)	1.443 (7)	Cl(2)–O(6)	1.317 (7)
Cl(2)–O(7)	1.397 (12)	N(1)–C(1)	1.494 (8)
N(1)–C(3)	1.487 (6)	N(1)–C(5)	1.520 (7)
N(2)–C(4)	1.498 (7)	N(3)–C(6)	1.487 (7)
N(4)–C(2)	1.490 (7)	C(1)–C(2)	1.519 (7)
C(3)–C(4)	1.523 (9)	C(5)–C(6)	1.521 (9)
C(7)–O(8)	1.255 (10)	C(7)–O(9)	1.286 (5)
N(1)–Cr–N(2)	82.4 (2)	N(1)–Cr–N(3)	83.3 (2)
N(2)–Cr–N(3)	91.7 (2)	N(1)–Cr–N(4)	83.1 (2)
N(2)–Cr–N(4)	164.7 (2)	N(3)–Cr–N(4)	91.7 (2)
N(1)–Cr–O(9)	90.9 (2)	N(2)–Cr–O(9)	87.2 (2)
N(3)–Cr–O(9)	174.2 (2)	N(4)–Cr–O(9)	87.9 (2)
N(1)–Cr–O(10)	174.5 (2)	N(2)–Cr–O(10)	96.7 (2)
N(3)–Cr–O(10)	91.3 (2)	N(4)–Cr–O(10)	98.2 (2)
O(9)–Cr–O(10)	94.5 (2)	O(1)–Cl(1)–O(2)	113.1 (3)
O(1)–Cl(1)–O(3)	110.4 (3)	O(2)–Cl(1)–O(3)	109.4 (3)
O(1)–Cl(1)–O(4)	108.1 (3)	O(2)–Cl(1)–O(4)	109.2 (4)
O(3)–Cl(1)–O(4)	106.3 (4)	O(5)–Cl(2)–O(6)	112.9 (4)
O(5)–Cl(2)–O(7)	106.5 (5)	O(6)–Cl(2)–O(7)	105.6 (5)
O(5)–Cl(2)–O(6A)	112.9 (4)	O(6)–Cl(2)–O(6A)	112.6 (6)
O(7)–Cl(2)–O(6A)	105.6 (5)	Cr–N(1)–C(1)	106.0 (3)
Cr–N(1)–C(3)	106.0 (3)	C(1)–N(1)–C(3)	111.7 (4)
Cr–N(1)–C(5)	110.2 (3)	C(1)–N(1)–C(5)	110.8 (4)
C(3)–N(1)–C(5)	111.9 (4)	Cr–N(2)–C(4)	111.7 (3)
Cr–N(3)–N(6)	109.7 (3)	Cr–N(4)–C(2)	110.8 (3)
N(1)–C(1)–C(2)	109.4 (5)	N(4)–C(2)–C(1)	110.0 (4)
N(1)–C(3)–C(4)	109.6 (4)	N(2)–C(4)–C(3)	109.1 (4)
N(1)–C(5)–C(6)	112.3 (4)	N(3)–C(6)–C(5)	109.1 (5)
O(8)–C(7)–O(9)	120.1 (3)	O(8)–C(7)–O(9A)	120.1 (3)
O(9)–C(7)–O(9A)	119.8 (7)	Cr–O(9)–C(7)	139.4 (4)
Cr–O(10)–CrA	131.5 (3)		

quisition was possible. The equipment for controlling and measuring temperature to within 0.1% is described in the literature.[20]

Luminescence was excited by the 488-nm line of a Spectra Physics 164 Ar ion laser, dispersed by a Spex 1404 double monochromator and detected by a cooled RCA C31034 photomultiplier. The signal was processed by an SRS SR530 lock-in amplifier. A liquid-helium immersion cryostat, built in the laboratory, was used to cool the sample to 1.5 K.

Results and Discussion

Synthesis. The reaction of [(tren)CrCl$_2$]Cl with silver perchlorate was initially carried out with the intention of producing a dihydroxo-bridged complex (**2**). However, the product that crystallized from the reaction mixtures (pH 7–9), albeit in low yield, was a binuclear complex containing both carbonato and hydroxo bridges (**1**). The IR spectrum showed bands at 1493,

[(tren)Cr(μ-OH)$_2$Cr(tren)](ClO$_4$)$_4 \cdot n$H$_2$O

2

↑ Δ

[(tren)CrCl$_2$]Cl + AgClO$_4$ ⟶ [(tren)Cr(OH)$_x$(OH$_2$)$_{2-x}$]$^{(3-x)+}$ + 3AgCl

↓ Δ, CO$_2$

[(tren)Cr(μ-CO$_3$)(μ-OH)Cr(tren)](ClO$_4$)$_3 \cdot$2H$_2$O

1
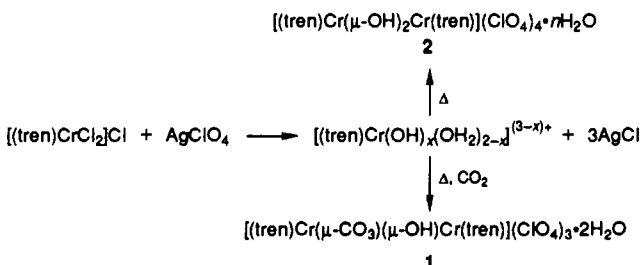
1376, 895, and 692 cm^{-1}, attributable to the presence of a bridging carbonate. It could be the case that this product is more insoluble or crystallizes more easily than other Cr(III) complexes present in the reaction mixture. Nevertheless, the complex represents another example of fixation of atmospheric CO$_2$ by a transition metal complex.

The yield of product was increased to about 65% by the addition of sodium bicarbonate to the solution of [(tren)Cr(OH)$_x$-(OH$_2$)$_{2-x}$]$^{(3-x)+}$. Even with this knowledge, the pathway for product formation cannot be assigned with certainty. Speciation of CO$_2$ and the Cr(III) complex in aqueous solution are major complicating factors. There are literature precedents for the

reaction of CO_2 with both bridging hydroxo,[15] oxo,[21] and peroxo[22] groups and terminal OH groups[23] which could be followed by substitution at Cr(III) to give the desired product. For example, the reaction of the [LCu(μ-OH)$_2$CuL] complex with atmospheric CO_2 to produce [LCu(μ-CO$_3$)CuL] involves attack of CO_2 by a bridging OH group followed presumably by other metal-centered substitution processes.[15] Many examples exist, particularly of Co(III) and Rh(III) complexes, where carbonato complexes are formed by reaction of CO_2 with terminal OH groups.[14,23] Such examples are rare in the case of Cr(III). The formation of [Cr(cycb)CO$_3$]$^+$ (cycb = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), which contains a chelating carbonate,[24] and [(tacn)Cr(μ-CO$_3$)(μ-OH)$_2$Cr(tacn)]$^{2+}$, which contains a bridging carbonate,[11] has been proposed to involve reaction of CO_2 with terminal OH groups. There is also the possibility that the product (1) could form by the reaction of mononuclear Cr(III) species with HCO_3^-, since most CO_2 would be present in this form in the pH range 7–9. However, there appears to be little experimental evidence supporting this proposal.

An alternative quite efficient synthesis of the product is as follows:

$$Cr^{2+} + tren \rightarrow [(tren)Cr(OH_2)_2]^{2+} \xrightarrow[\text{2. } O_2]{\text{1. NaHCO}_3} 1$$
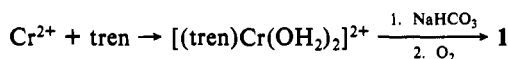
Presumably, the formation of the OH bridge is associated with the oxidation process and is likely to go through a Cr(IV) intermediate.[17,25] It is not clear, however, whether oxidation occurs before or after attachment of the carbonato group. Although addition of sodium bicarbonate to [(tren)Cr(OH$_2$)$_2$]$^{2+}$ solutions produces no obvious change in color, this does not exclude the possibility of carbonate coordination at this stage, since this would cause little perturbation to the primary coordination sphere of Cr(II). Note that, in this case, the product formed without heating of the reaction mixtures.

Molecular Structure of [(tren)Cr(μ-OH)(μ-CO$_3$)Cr(tren)]-(ClO$_4$)$_3$·2H$_2$O. The structure of [(tren)Cr(μ-OH)(μ-CO$_3$)Cr-(tren)](ClO$_4$)$_3$·2H$_2$O consists of discrete dimeric cations in which two Cr(III) centers are linked by one carbonato and one hydroxo group, with nitrogen atoms from the ligand completing the distorted octahedral geometry about each metal center (Figure 1). The mode of coordination of the carbonate anion is identical to that found in [(tacn)Cr(μ-OH)$_2$(μ-CO$_3$)Cr(tacn)]$^{2+}$,[11] *trans*-[(NH$_3$)(cyclam)Cr(μ-CO$_3$)Cr(cyclam)(NH$_3$)]$^{4+}$,[10] and some Fe(III) complexes[5,6] but different from that adopted in some Cu(II) complexes where all three oxygens are coordinated to copper.[8]

The C–O distances within the carbonate anion, 1.286 and 1.255 Å to bound and free oxygen atoms, respectively, the M–O(CO$_3$) distances of 1.954 Å, and the M–O(OH) distance of 1.944 Å (Table III), are in agreement with those reported for [(tacn)-Cr(μ-OH)$_2$(μ-CO$_3$)Cr(tacn)]$^{2+}$.[11] However, the M–O(CO$_3$) distances are shorter than for acetato-bridged complexes,[7,26] a reflection of the higher charge and, hence, stronger binding ability of carbonate. These groups have little effect on M–OH distances within the bridging moiety. The Cr···Cr distance (3.56 Å) is much longer than in typical bis(hydroxo) complexes (ca. 3 Å) but approaches that in singly bridged complexes of the type [LCr(μ-OH)CrL]$^{5+}$, where Cr···Cr $\approx$ 3.6–3.9 Å.[27] A corresponding increase in M···M distance is observed in going from the tris-(hydroxo) complex [(Me$_3$tacn)Cr(μ-OH)$_3$Cr(Me$_3$tacn)]$^{3+}$ (Cr···Cr = 2.64 Å)[3a] to the bis(hydroxo) carbonate complex cited above (Cr···Cr = 2.9 Å).[11] In the title compound (1), the carbonato
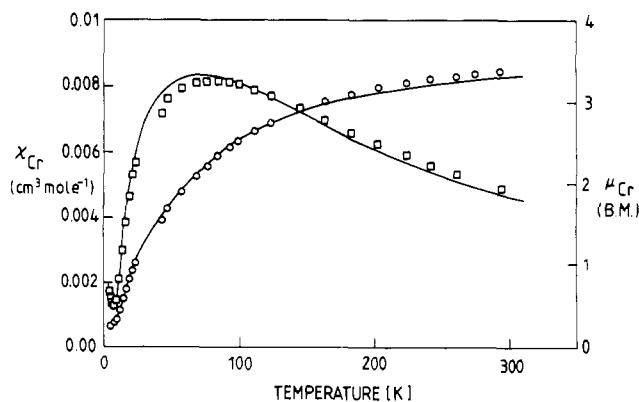

Figure 2. Temperature dependence of the molar magnetic susceptibility ($\square$, experimental; —, calculated) and effective magnetic moment (O, experimental, —, calculated) of [(tren)Cr(μ-OH)(μ-CO$_3$)Cr(tren)]-(ClO$_4$)$_3$·2H$_2$O.

group causes a widening of the M–OH–M angle (Table III) to well above those commonly found in bis(hydroxo) complexes (ca. 100°).[27] Similar enlargements have been reported for dibridged complexes containing one carboxylato and either an oxo or a hydroxo group.[26] As will be discussed later, these variations in bond angles and distances have a pronounced effect on M···M interactions.

An interesting structural feature of complex 1 is the disposition of the carbonato group trans to a primary nitrogen. The Cr–N distances are all equal and provide little insight into the adopted stereochemistry. Mechanistic information would assist in the rationalization of this observation. Information on other complexes of tetradentate ligands does not present a clearer picture. In [(tmpa)Cr(μ-O)(μ-CO$_2$CH$_3$)Cr(tmpa)]$^{3+}$[26] and in the analogous Fe(III) carbonato and acetato complexes,[7] the acetate and carbonate bridges are trans to a pyridyl nitrogen on one metal center and trans to the tertiary nitrogen on the other.

Electronic Spectrum. The UV–vis spectrum of complex 1 in 1 M HClO$_4$ is typical of octahedral Cr(III) complexes, showing two spin-allowed transitions from $^4A_{2g}$ to $^4T_{2g}$ and $^4T_{1g}$ at 504 and 392 nm, respectively. In 1 M NaOH, however, other transitions are observed in addition to bands corresponding to the spin-allowed transitions at 598 and 445 nm. These spectral changes can be rationalized in terms of the conversion of the bridging OH group into an oxo group, i.e. the generation of [(tren)Cr(μ-CO$_3$)(μ-O)Cr(tren)]$^{2+}$. The spin-allowed bands have shifted to lower energy, as is expected from the lower ligand field strength of the oxo ligand. Similar changes in spectrum have been observed on addition of base to other hydroxo-bridged binuclear complexes of Cr(III).[26,27] The most striking feature of the spectrum is the substantial enhancement of the spin-forbidden transitions which occur at 725, 690, and 508 nm. These bands can be assigned to transitions between the ground state, which through the exchange mechanism has mixed character (i.e. it no longer behaves as a pure $^4A_{2g}$ ground state), and the various excited states. Attempts to obtain crystalline salts of the oxo complex are in progress. This cannot be achieved by reaction in basic aqueous solution because the complex undergoes relatively rapid hydrolysis producing in the first instance a mononuclear hydroxo complex, [(tren)Cr-(OH)$_2$]$^+$ (λ_{max} = 575 and 408 nm), followed by further reaction to give polynuclear Cr(III) species. As expected, the spectral features attributed to spin-forbidden transitions in the oxo-bridged dimer are no longer obvious in the spectrum of [(tren)Cr(OH)$_2$]$^+$.

Magnetic Susceptibility. The solid-state magnetic susceptibility of a powdered sample of the complex was measured at 10 kG and in the temperature range 4.2–300 K. Plots of molecular susceptibility, χ_M (per Cr), and μ_{eff} against temperature are shown in Figure 2. Linear least-squares analysis was used to fit the data to a susceptibility expression based on the isotropic spin Hamiltonian:[28]

$$H = -2JS_1 \cdot S_2 \qquad S_1 = S_2 = \tfrac{3}{2}$$

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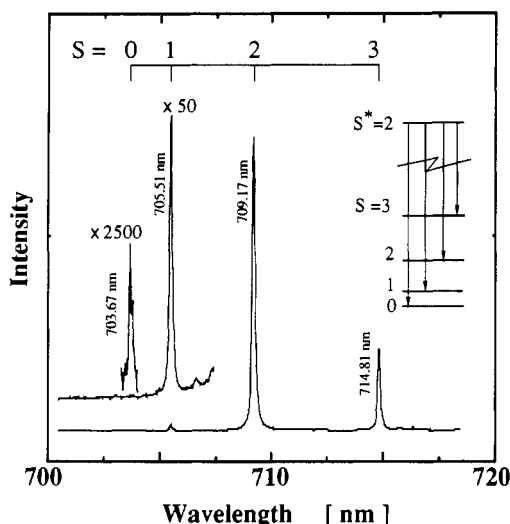
Figure 3. Unpolarized luminescence spectrum of a single crystal of $[(tren)Cr(\mu\text{-OH})(\mu\text{-CO}_3)Cr(tren)](ClO_4)_3 \cdot 2H_2O$ recorded at 1.5 K showing the wavelengths and relative intensities of the transitions. The spin quantum numbers of the lowest excited state ($S^* = 2$) and the final ground state ($S = 0, 1, 2, 3$) are denoted.

There was no need to introduce a term allowing for the presence of magnetostriction which has sometimes been necessary in other systems.[2] However, allowance was made for the presence of a paramagnetic impurity (ca. 0.5%) by introducing a Curie–Weiss term. The J value of -16.8 cm^{-1} obtained from this treatment indicates weak antiferromagnetic coupling between the metal centers, which is responsible for a substantial decrease in the magnetic moment below 100 K. The value of J is slightly smaller but is still in good agreement with that obtained from luminescence spectra.

Luminescence Spectrum. The luminescence spectrum of a single crystal of $[(tren)Cr(\mu\text{-OH})(\mu\text{-CO}_3)Cr(tren)](ClO_4)_3 \cdot 2H_2O$ is shown in Figure 3. The sharpness of the lines indicates that the compound has a well-defined structure; i.e., only minute structural deviations are observed from site to site.[29] All four transitions from the luminescent lowest excited state to the spin levels of the exchange-split ground state ($S = 0, 1, 2, 3$) are observed. Their wavelength is indicated in Figure 3. The intensity distribution shows that the transition to the $S = 2$ ground state is the most intense. Thus, we can conclude that the lowest excited state is a spin quintet ($S^* = 2$)[29] and that the line corresponds to the spin-allowed transition $S^* = 2 \rightarrow S = 2$. The other lines in the spectrum ($S^* = 2 \rightarrow S = 0, 1, 3$) are weaker in intensity because of a change in the spin quantum number. Indeed, the title compound is one of few complexes for which the doubly spin-forbidden transitions (e.g. $S^* = 2 \rightarrow S = 0$) have been observed.

The isotropic spin Hamiltonian for a chromium(III) dimer (ground state $^4A_2{}^4A_2$) leads to a Landé pattern with energy separations of $2J$, $4J$, and $6J$ between the spin levels $S = 0$ and $S = 1$, $S = 1$ and $S = 2$, and $S = 2$ and $S = 3$, respectively.[30] The energy difference between the four observed transitions (Figure 3) indeed shows a Landé pattern from which we deduce a value of -18.5 (± 0.1) cm^{-1} for the exchange parameter J. The deviations from the Landé pattern are exceptionally small, further confirming that modification of the operator to include a biquadratic expression describing the effect of magnetostriction is unnecessary. This was definitely not the case for the related complex $[(bisbicam)Cr(\mu\text{-OH})(\mu\text{-SO}_4)Cr(bisbicam)](S_2O_6) \cdot 3H_2O$ (bispicam = bis(2-pyridylmethyl)amine) where a large j value ($\sim 14\%$ of J) was found.[31] Thus, the carbonato complex reported

here must have an extremely rigid structure which is not vulnerable to magnetostriction.

Interpretation of Magnetic Properties. The understanding of magnetic interactions in binuclear Cr(III) complexes is not as well advanced as for analogous Cu(II) complexes although the Glerup–Hodgson–Pedersen model[32] successfully rationalizes magnetic interactions in many hydroxo-bridged binuclear Cr(III) complexes. Several factors have emerged that influence M···M interactions[2,32] which also apply in the Cr(III) case. These include the M···M distance (for short M···M distances the direct exchange mechanism dominates the superexchange mechanism, as is the case for $[(Me_3tacn)Cr(\mu\text{-OH})_3Cr(Me_3tacn)]I_3$,[30] while the converse is true when the M···M separation is much longer), M–O bond distance, M–O–M angle, tilt angle (for hydroxo-bridged complexes the angle of the O–H bond out of the M–O–M plane is believed to be important), and crystal packing effects. Coupling between Cr(III) centers is generally antiferromagnetic, and to our knowledge there are only two complexes which show very weak ferromagnetism (Table IV).

The strength of antiferromagnetic coupling between the Cr(III) centers in the carbonato complex (1), $J = -18.5$ cm^{-1}, is typical of dihydroxo-bridged complexes containing nitrogenous ligands ($J = 0 \rightarrow -25$ cm^{-1}) but, as expected, weaker than in oxo-bridged complexes (see Table IV). The similar strengths of the Cr···Cr couplings for the carbonato complex and tetraamine diols with identical Cr–O distances probably arises from compensation between two opposing effects. The longer Cr···Cr distance in the carbonato complex (3.56 Å; cf. ~ 3 Å) should result in weaker direct coupling, and this is offset by an expansion in the Cr–O–Cr angle from ~ 100 to $132°$, which allows better overlap of p- and d-orbitals and facilitates Cr···Cr communication. This is further highlighted by the monohydroxo-bridged complex $[(NH_3)_5Cr(\mu\text{-OH})Cr(NH_3)_5]Cl_5 \cdot H_2O$, which has the same J value (-16 cm^{-1}) as the carbonato complex, despite a much longer Cr···Cr distance of 3.85 Å.[33] Once again, an enlargment in the M–O–M

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Table IV. Structural and Magnetic Data for Binuclear Cr(III) Complexes

complex	Cr···Cr, Å	Cr–O–Cr,[a] deg	Cr–O(s),[b] Å	$-J$, cm^{-1}	ref
[(H$_2$O)$_4$Cr(OH)$_2$Cr(OH$_2$)$_4$](dmtos)$_4$·4H$_2$O[c]	3.006	101.8	1.936	−5.0	34
Na$_4$[(mal)$_2$Cr(OH)$_2$Cr(mal)$_2$]·5H$_2$O[d]	3.031	99.3	1.988	−1.1	32, 35
Na$_4$[(ox)$_2$Cr(OH)$_2$Cr(ox)$_2$]·6H$_2$O[e]	3.000	99.6	1.963	0.3	36
[(NH$_3$)$_4$Cr(OH)$_2$Cr(NH$_3$)$_4$]Cl$_4$·4H$_2$O, triclinic	3.041	100.8	1.973	0.7	37
[(en)$_2$Cr(OH)$_2$Cr(en)$_2$](S$_2$O$_6$)$_2$[f]	3.031	100.0	1.979	1.7	32, 38
[(gly)$_2$Cr(OH)$_2$Cr(gly)$_2$][g]	2.974	98.2	1.967	1.9	39
[(NH$_3$)$_4$Cr(OH)$_2$Cr(NH$_3$)$_4$]Cl$_4$·4H$_2$O, monoclinic	3.023	99.9	1.965	2.1	32, 40
[(cyclam)Cr(CO$_3$)Cr(cyclam)](S$_2$O$_6$)$_2$·3H$_2$O[h]	5.964	101.8	1.948	2.6	41
[(NH$_3$)$_4$Cr(OH)$_2$Cr(NH$_3$)$_4$](S$_2$O$_6$)$_2$·4H$_2$O	3.045	101.5	1.975	2.9	32, 40
[(Br-acac)$_2$Cr(OMe)$_2$Cr(Br-acac)$_2$][i]	3.039	101.5	1.962	4.3	32, 42
[(acac)$_2$Cr(OMe)$_2$Cr(acac)$_2$][j]	3.028	101.0	1.962	4.8	32, 43
[(Cl-acac)$_2$Cr(OMe)$_2$Cr(Cl-acac)$_2$][k]	3.025	101.1	1.959	4.9	32, 44
[(Cl-dipic)(H$_2$O)Cr(OH)$_2$Cr(OH$_2$)(Cl-dipic)][l]	2.997	100.7	1.947	5.1	32, 45
[(bispicam)Cr(OH)$_2$(SO$_4$)Cr(bispicam)]S$_2$O$_6$·3H$_2$O[m]	2.916	97.0	1.946	7.5	31, 46
[Br-acac)$_2$Cr(OEt)$_2$Cr(Br-acac)$_2$][i]	3.028	101.8	1.951	9.0	32, 42
[(HO)(NH$_3$)$_4$Cr(OH)Cr(NH$_3$)$_5$](S$_2$O$_6$)$_2$·3H$_2$O	3.744	142.8	1.962	10.3	47
[(cyclen)Cr(OH)$_2$Cr(cyclen)](S$_2$O$_6$)$_2$·4H$_2$O[n]	3.086	104.1	1.957	10.8	48
[(H$_2$O)$_3$Cr(OH)(O$_2$CH)$_2$Cr(OH$_2$)$_3$](tos)$_3$·2H$_2$O[o]	3.381	123.4	1.920	11.2	49
[(bispicen)Cr(OH)$_2$(bipicen)](ClO$_4$)$_4$·H$_2$O[p]	3.046	103	1.946	11.9	50
[(en)$_2$Cr(OH)$_2$Cr(en)$_2$]Cl$_2$(ClO$_4$)$_2$[f]	3.06	103.4	1.949	13.4	32, 51, 52
[(en)$_2$Cr(OH)$_2$Cr(en)$_2$]Br$_4$·2H$_2$O[f]	3.038	102.6	1.946	15.0	52, 53
[(tmpa)Cr(OH)$_2$Cr(tmpa)](ClO$_4$)$_4$·4H$_2$O[q]	3.003	100.5	1.953	15.3	25, 54, 55
[(NH$_3$)$_5$Cr(OH)Cr(NH$_3$)$_5$]Cl$_5$·H$_2$O	3.852	165.9	1.941	15.8	33
[(bispictn)Cr(OH)$_2$Cr(bispictn)](ClO$_4$)$_4$·3H$_2$O[r]	3.054	102.0	1.964	16.3	56
[(2-picetam)Cr(OH)$_2$Cr(2-picetam)](S$_2$O$_6$)$_2$·2H$_2$O[s]	3.019	102.3	1.938	16.5	32, 57
trans-[(NH$_3$)$_4$(H$_2$O)Cr(OH)Cr(NH$_3$)$_5$]Cl$_5$·3H$_2$O	3.872	155.1	1.983	17.3	58
[(tren)Cr(OH)(CO$_3$)Cr(tren)](ClO$_4$)$_3$·2H$_2$O[t]	3.560	131.5	1.944	18.5	this work
[(phen)$_2$Cr(OH)$_2$Cr(phen)$_2$]Cl$_4$·6H$_2$O[u]	3.018	103.1	1.927	21.5	32, 59
[(phen)$_2$Cr(OH)$_2$Cr(phen)$_2$]I$_4$·4H$_2$O[u]	2.986	102.1	1.919	21.8	59
Complexes with Short Cr···Cr Distances					
[Cr$_2$(OH)$_2$(O$_2$CCH$_3$)tpen](ClO$_4$)$_3$[v]	2.818	93.1	1.943	33.5	60
(NEt$_4$)[Cr$_2$(OEt)$_3${H$_2$B(pz)$_2$}(NCS)$_2$][w]	2.683	87.4	1.943	43.5	61
[(tacd)Cr(OH)$_3$Cr(tacd)]Br$_3$·2H$_2$O[x]	2.666	84.4	1.98	48	62, 63
[(NH$_3$)$_3$Cr(OH)$_3$Cr(NH$_3$)$_3$](ClO$_4$)$_{3-x}$I$_x$	2.631	83.6	1.973	59.5	64
[(Metacn)Cr(OH)$_3$Cr(Metacn)]I$_3$·3H$_2$O[y]	2.642	84.1	1.972	64	30, 65, 66
[(tacn)Cr(OH)$_3$Cr(tacn)](ClO$_4$)$_3$·3H$_2$O[z]	2.66		1.98	64.3	63
Oxo-Bridged Complexes					
[(2-picetam)$_2$CrO(OH)Cr(2-picetam)$_2$]Br$_3$·5H$_2$O[s]	2.883	100.6	1.875	23.2	67
[(Metacn)CrO(O$_2$CCH$_3$)$_2$Cr(Metacn)](BPh$_4$)$_2$[y]	3.219	121.0	1.85	28	68
[(2-picetam)CrO$_2$Cr(2-picetam)]Cl$_2$[s]	2.80	95.5	1.890	42	32, 67
[(tmpa)CrO(O$_2$CCH$_3$)Cr(tmpa)](ClO$_4$)$_3$[q]	3.33	132	1.821	50.3	25
[(NH$_3$)$_5$CrOCr(NH$_3$)$_5$]Cl$_4$·H$_2$O	3.63	180	1.815	225	32, 69, 70
[(tmpa)(NCS)CrOCr(NCS)(tmpa)](ClO$_4$)$_2$·^{1}/$_2$H$_2$O[q]	3.600	180	1.80	255	71

[a] Average Cr–O–Cr angle for hydroxo or oxo linkage with shortest Cr–O distance. [b] Cr–O(s) = shortest average Cr–O distance within bridging unit. [c] dmtos = mesitylene-2-sulfonic acid. [d] mal = malonato. [e] ox = oxalato. [f] en = ethylenediamine. [g] gly = glycinato. [h] cyclam = 1,4,8,11-tetraazacyclotetradecane. [i] Br-acac = bromoacetylacetonato. [j] acac = acetylacetonato. [k] Cl-acac = chloroacetylacetonato. [l] Cl-dipic = 4-chloropyridine-2,6-dicarboxylato. [m] bispicam = bis((2-pyridylmethyl)amine). [n] cyclen = 1,4,7,10-tetraazacyclododecane. [o] tos = *p*-toluenesulfonate. [p] bispicen = *N*,*N*′-bis(2-pyridylmethyl)-1,2-ethanediamine. [q] tmpa = tris(2-pyridylmethyl)amine. [r] bispictn = *N*,*N*′-bis(2-pyridylmethyl)-1,3-propanediamine. [s] 2-picetam = 1-(2-pyridyl)ethylamine. [t] tren = bis(2-aminoethyl)ethane-1,2-diamine. [u] phen = 1,10-phenanthroline. [v] tpen = *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,2-ethanediamine. [w] H$_2$B(pz)$_2$ = dihydrobis(1-pyrazolyl)borate. [x] tacd = 1,5,9-triazacyclododecane. [y] Metacn = 1,4,7-trimethyl-1,4,7-triazacyclononane. [z] tacn = 1,4,7-triazacyclononane.

angle seems to compensate for the longer distance over which interaction must occur.

Encouraged by the success of Gorun and Lippard's correlation of magnetic interactions in binuclear Fe(III) complexes with the average shortest Fe–O distance,[4] we undertook an examination of existing magnetic and structural information on related Cr(III) complexes (see Table IV). A quantitative relationship cannot be developed at this stage because although the relevant information is available for many hydroxy-bridged complexes (shortest Cr–O distances = Cr–O(s) > 1.9 Å), few complexes are known which have the Cr–O(s) < 1.9 Å. Nevertheless, a number of observations

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can be made about the data in Table IV: (i) The coupling constants for several complexes with Cr···Cr distances of or below 2.8 Å are significantly higher in magnitude than those for complexes with Cr···Cr distances greater than 3 Å, for a given Cr–O(s) value. This is consistent with the existence of a direct exchange pathway. Note that the Fe···Fe distances were greater than 3 Å for all complexes used in the Fe(III) correlation.[4] (ii) Linear oxo-bridged complexes show much stronger coupling than complexes with bent bridges of similar Cr–O(s). Interestingly, the Fe(III) correlation applies to doubly and triply bridged complexes and excludes linear complexes.[4] (iii) Apart from these cases, the data do show an increase in the magnitude of J with decreasing

Cr–O(s) similar to that found for the Fe(III) complexes. Clearly, there is a need for further work aimed at the isolation of oxo-bridged Cr(III) complexes in particular containing bent Cr–O–Cr units.

Supplementary Material Available: For **1**, anisotropic displacement coefficients (Table S1) and H atom coordinates and isotropic displacement coefficients (Table S2) (1 page); a listing of structure factors (Table S3) (10 pages). Ordering information is given on any current masthead page.

Substituent Constant Correlations as Predictors of Spectroscopic, Electrochemical, and Photophysical Properties in Ring-Substituted 2,2'-Bipyridine Complexes of Rhenium(I)

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The synthesis and the spectroscopic, electrochemical and photophysical properties of the homologous series of photosensitizers, *fac*-[4,4'-X₂-5,5'-Y₂-2,2'-bipyridine]Re(CO)₃Etpy⁺ (X = NEt₂, Me, OMe, H, Ph, Cl, CO₂Me, NO₂, Y = H; X = Y = Me; Etpy = 4-ethylpyridine) are described. Both the quasi-reversible or irreversible oxidation of the Re(I) center and the reversible or quasi-reversible, one-electron reduction of the coordinated bipyridyl ligand are observed to vary with the electron donor/acceptor abilities of X, Y as measured by the sum of the Hammett substituent constants $\sigma_m + \sigma_p$. Hammett ($\sigma_T = \sigma_p + \sigma_m$) values for the X, Y groups are observed to correlate linearly with the metal-to-ligand charge-transfer (MLCT) absorption and emission energies and provide a convenient tool for the estimation of excited-state properties of the complexes. The complexes are moderately strong excited-state oxidants ($E_{1/2}(+^*/0)$ = 0.73–1.12 V vs SSCE) and exhibit emission maxima in the range 528 nm (X = NEt₂, Y = H) to 755 nm (X = NO₂, Y = H). MLCT excited-state decay is dominated by nonradiative decay from the ³MLCT state to the ground state and is governed by an "energy gap law". It is shown that excited-state properties such as absorption energy, emission energy, rate of nonradiative decay (k_{nr}), and the rate of radiative decay (k_r) correlate with σ_T. The correlations can be derived from more fundamental considerations. The dependence of ln k_{nr} on emission energy is similar to values obtained in earlier studies with bipyridyl Ru(II) or Os(II) complexes which do not contain coordinated CO and somewhat less than that observed in a previous study for *fac*-(bpy)Re(CO)₃(L')⁺ complexes (L' = monodentate, neutral ligands). This behavior is interpreted as an indication that nonradiative decay involves acceptor modes that are predominantly ring-based vibrations of the substituted bipyridine ligand, but that CO modes are also involved.

Introduction

Complexes of 2,2'-bipyridine (bpy) and its derivatives with spin-paired d⁶ third-row transition metals such as Os(II),[1–6] Ir-(III),[7,8] and Re(I)[9–15] have received increasing attention due, at least in part, to the potential versatility of such compounds as catalysts[2–14,16–19] and as sensitizers in solar energy conversion[9–11,15,20] schemes. One particularly promising class of compounds for these applications are the *fac*-[L]Re(CO)₃(L')ⁿ⁺ (L = 2,2'-bipyridine, and 1,10-phenanthroline and its substituted derivatives; L' = Cl⁻, n = 0; L' = PMe₃, pyridine, MeCN, and other neutral monodentate ligands; n = 1) complexes. The L' = Cl⁻ complexes have been found to act as catalysts for the reduction of carbon dioxide in homogeneous solution[12–14,16–18] and as catalysts bound to electrode surfaces.[17–19] The importance of the *fac*-[L]Re-(CO)₃(L')ⁿ⁺ complexes as sensitizers in solar energy storage schemes has long been recognized.[9–11,20] Luminescence originating from the relaxation of the metal-to-ligand charge-transfer (MLCT) excited state to the ground state provides a convenient probe of photophysical decay channels. These properties have been exploited to obtain information concerning the mechanisms of intramolecular electron-transfer reactions.[21–23] In addition, the sensitivity of photophysical properties to the local solution

environment has also been exploited[24,25] to determine the nature of intermolecular interactions of *fac*-(bpy)Re(CO)₃NC-

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