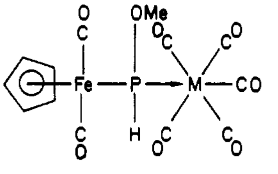
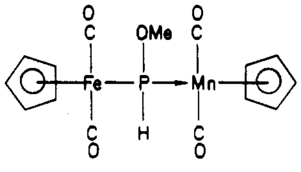
stepwise by the other groups of interest and suggests potential synthetic applications of these systems in organophosphorus coordination chemistry.

Some methanolysis reactions were also investigated. Thus, treatment of $CpFe(CO)_2PHClM(CO)_5$ (M = Cr, W) with boiling methanol gives the corresponding $CpFe(CO)_2PH(OMe)M(CO)_5$ derivatives, VI. A manganese analogue, $CpFe(CO)_2PH(OMe)Mn(CO)_2Cp$ (VII), was prepared directly from $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Mn(CO)_2Cp$ by heating in boiling methanol. The patterns of the ν(CO) frequencies of these methoxy derivatives (Table II) resemble those of the analogous diisopropylamino and halo derivatives. The proton NMR spectra of these methoxy derivatives exhibit the expected doublet OCH_3 resonances around δ 3.5–3.6 (J = 12–13 Hz) in addition to the PH and C_5H_5 resonances.


VI


VII

Acknowledgment. We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AFOSR-84-0050.

Registry No. $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Cr(CO)_5$, 97825-67-7; $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Mo(CO)_5$, 97825-68-8; $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)W(CO)_5$, 97825-69-9; $NaFe(CO)_2Cp$, 12152-20-4; $[CpFe(CO)_2]_2$, 12154-95-9; $i\text{-}Pr_2NP(H)BrCr(CO)_5$, 102283-12-5; $i\text{-}Pr_2NP(H)ClMo(CO)_5$, 102260-82-2; $i\text{-}Pr_2NP(H)ClW(CO)_5$, 102260-83-3; $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Mn(CO)_2Cp$, 97825-75-7; $i\text{-}Pr_2NP(H)ClMn(CO)_2Cp$, 102260-84-4; $CpFeCr(CO)_6PH(N\text{-}i\text{-}Pr_2)$, 102260-85-5; $CpFeW(CO)_6PH(N\text{-}i\text{-}Pr_2)$, 102260-86-6; $Cp_2FeMn(CO)_3PH(N\text{-}i\text{-}Pr_2)$, 97825-76-8; $CpFe(CO)_2PHClCr(CO)_5$, 102260-87-7; $CpFe(CO)_2PHBrCr(CO)_5$, 102260-88-8; $CpFe(CO)_2PHClMo(CO)_5$, 102260-89-9; $CpFe(CO)_2PHBrMo(CO)_5$, 102260-90-2; $CpFe(CO)_2PHClW(CO)_5$, 102260-91-3; $CpFe(CO)_2PHBrW(CO)_5$, 97825-71-3; $CpFe(CO)_2PH(OMe)Cr(CO)_5$, 102260-92-4; $CpFe(CO)_2PH(OMe)W(CO)_5$, 102260-93-5; $CpFe(CO)_2PH(OMe)Mn(CO)_2Cp$, 102260-94-6; Fe, 7439-89-6; W, 7440-33-7; Cr, 7440-47-3; Mn, 7439-96-5; Mo, 7439-98-7.

Supplementary Material Available: Listings of anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

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Electron-Transfer Barriers in Cobalt(III) and Cobalt(II) Bis Complexes of 1,4,7-Triazacyclononane (tacn) and 1,4,7-Trithiacyclononane (ttcn). Crystal Structures of $[Co^{II}(tacn)_2]I_2{\cdot}2H_2O$ and of $[Co^{III}(ttcn)_2](ClO_4)_3$

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The structures of $[Co(tacn)_2]I_2{\cdot}2H_2O$ and of $[Co(ttcn)_2](ClO_4)_3$ have been determined, where tacn is 1,4,7-triazacyclononane ($C_6H_{15}N_3$) and ttcn is 1,4,7-trithiacyclononane ($C_6H_{12}S_3$). The cobalt(II) complex crystallizes in the orthorhombic crystal system, space group *Ibca* (D_{2h}^{27}), with a = 13.60 (2) Å, b = 15.43 (1) Å, c = 20.81 (2) Å, and Z = 8. The structure was refined to a conventional R value of 0.067. The coordination sphere consists of six nitrogen atoms of two tacn ligands in a distorted octahedral arrangement about the cobalt(II). The average Co–N distance is 2.155 Å. The cobalt(III) complex crystallizes in the monoclinic crystal system, space group $C2/c$ (C_{2h}^{6}), with a = 12.194 (3) Å, b = 15.146 (4) Å, c = 13.418 (3) Å, β = 94.42 (2)°, and Z = 4. The structure was refined to R = 0.0395. The coordination sphere consists of six sulfur atoms of two ttcn ligands in a nearly regular octahedral arrangement about the cobalt(III). The average Co–S distance is 2.253 Å. The electron-exchange rate constant for the reaction of $[((R)\text{-Metacn})Co(tacn)]^{2+}$ and $[((S)\text{-Metacn})Co(tacn)]^{3+}$ has been determined ($k_{ex} = 0.19$ M^{-1} s^{-1} at 25 °C; I = 0.1 M ($LiClO_4$)). The corresponding rate constant for the couple $[Co(ttcn)_2]^{3+/2+}$ has been evaluated to be 1.3×10^4 M^{-1} s^{-1} at 25 °C (I = 0.2 M) from the cross-reaction between $[Co(ttcn)_2]^{3+}$ and $[Co(phen)_3]^{2+}$. The redox reactivities of $[Co(tacn)_2]^{3+/2+}$ and $[Co(ttcn)_2]^{3+/2+}$ have been analyzed in the frame of the Marcus–Sutin model for outer-sphere electron-transfer reactions.

Introduction

In the past 5 years a variety of complexes of first transition series metals containing two tridentate macrocyclic ligands such as 1,4,7-triazacyclononane (tacn) have been synthesized and have in many instances been characterized spectroscopically and crystallographically. The most remarkable property of these complexes is their pronounced stability in aqueous solution toward ligand dissociation. Thus, $[Ni(tacn)_2]^{2+}$ [2] and $[Ni(tacn)_2]^{3+}$,[3,4] $[Fe(tacn)_2]^{2+}$ [3,5] and $[Fe(tacn)_2]^{3+}$,[3,5] and $[Co(tacn)_2]^{2+}$ [3] and $[Co(tacn)_2]^{3+}$ [6] have been synthesized. The Ni[2,7] and Fe[5] pairs have been studied by X-ray crystallography, and metrical information concerning the metal–ligand distances is available. It is the change of these distances in changing the oxidation state of the central metal ion that governs the redox reactivity of these complexes. Electron-transfer rates are currently successfully analyzed by using a semiclassical model developed by Marcus and Sutin.[8-10]

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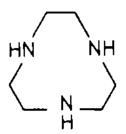
0020-1669/86/1325-2400$01.50/0

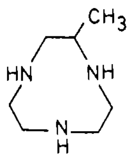
Table I. Crystallographic Data and Data Collection Parameters at 22 °C

	$[Co(tacn)_2]I_2 \cdot 2H_2O$	$[Co(ttcn)_2](ClO_4)_3$
formula	$C_{12}H_{34}N_6CoI_2O_2$	$C_{12}H_{24}S_6CoCl_3O_{12}$
fw	607.2	718
space group	*Ibca* (D_{2h}^{27})	*C*2/*c* (C_{2h}^{6})
a, Å	13.60 (2)	12.194 (3)
b, Å	15.43 (1)	15.146 (4)
c, Å	20.81 (2)	13.418 (3)
β, deg		95.42 (2)
V, Å^3	4367	2467.1
Z	8	4
d_{calcd}, g/cm^3	1.85	1.93
cryst size, mm^3	0.4 × 0.35 × 0.40	0.25 × 0.25 × 0.3
μ(Mo Kα), cm^{-1}	34.1	14.8
transmissn range (min–max)	0.227–0.376	0.56–0.65
diffractometer	AED II (Siemens)	AED II (Siemens)
radiation	Mo Kα (graphite monochromator)	Mo Kα (graphite monochromator)
scan method; type, deg	ω; $2.5 < 2\theta < 62$	ω; $2.5 < 2\theta < 62$
no. of reflcns	981	2648
no. of unique data ($I > 2.0\sigma(I)$)	870	2480
no. of variables refined	75	164
max shift/esd, final cycle	0.25	2.19 (O16 of disordered ClO_4), av 0.15
R	0.067	0.039
R_w	0.055	0.037

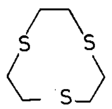
In this paper we wish to report the syntheses, characterization, and redox reactivities of such complexes of cobalt(II/III). We have used the macrocyclic ligands 1,4,7-triazacyclononane, (*R*)- and (*S*)-2-methyl-1,4,7-triazacyclononane, and 1,4,7-trithiacyclononane and have prepared their bis complexes of Co(II) and Co(III). The electron-exchange rate constant between $[((R)\text{-Metacn})Co(tacn)]^{2+}$ and $[((S)\text{-Metacn})Co(tacn)]^{3+}$ has been measured (0.19 M^{-1} s^{-1} at 25 °C; $I = 0.1$ M ($LiClO_4$)). $[Co(ttcn)_2](ClO_4)_3$ has been prepared for the first time, and its structure has been determined by X-ray crystallography. In addition, the structure of $[Co(tacn)_2]I_2 \cdot 2H_2O$ has also been determined.



tacn



(R)-Metacn or
(S)-Metacn



ttcn

Electron-transfer rates have been measured and analyzed in the frame of the Marcus–Sutin model.

Experimental Section

The ligands 1,4,7-triazacyclononane (tacn),[11] 1,4,7-trithiacyclononane (ttcn),[12] and (−)-(*R*)-2-methyl-1,4,7-triazacyclononane ((R)-Metacn)[13] were prepared as described in the literature. The ligand (+)-(*S*)-2-methyl-1,4,7-triazacyclononane was synthesized from (+)-(*S*)-diaminopropane[14] (optical purity 99.2%), which was N-tosylated and converted to its disodium salt. This disodium salt was heated with the tritosylate of diethanolamine in DMF at 100 °C for 2 h to give the cyclic tritosylate of (*S*)-2-methyl-1,4,7-triazacyclononane, which was detosylated in concentrated H_2SO_4 and converted to the free ligand in the usual manner.[11]

The following complexes were prepared according to procedures described in the literature: $[Co(phen)_3]Cl_2 \cdot 2H_2O$;[15] $[Co(tacn)_2]Br_3$;[6] $[Co(ttcn)_2](ClO_4)_2$;[17] $[((R)\text{-Metacn})Co(tacn)]Cl_3 \cdot 5H_2O$.[16]

Table II. Atomic Coordinates (×10^3) of $[Co(tacn)_2]I_2 \cdot 2H_2O$

atom	*x*	*y*	*z*
I	155.7 (1)	362.7 (1)	91.13 (7)
Co	500	250	131.1 (2)
N1	486 (1)	353 (1)	198.4 (7)
N2	523 (1)	144 (1)	62.4 (6)
N3	350 (1)	204.5 (9)	130.4 (6)
C1	418 (2)	416 (1)	169 (1)
C2	548 (2)	65 (1)	98 (1)
C3	425 (1)	138 (2)	30.2 (8)
C4	338 (1)	140 (1)	77.8 (8)
C5	333 (1)	170 (1)	193.1 (9)
C6	583 (1)	391 (1)	213 (1)
O_w	83 (1)	161.4 (8)	163.2 (6)

$[Co(tacn)_2]I_2 \cdot 2H_2O$. The volume of a solution of $CoCl_2 \cdot 6H_2O$ (1 g) in dimethyl sulfoxide (25 mL) was reduced to 20 mL at 190 °C in order to minimize the amount of water. This solution was purged with argon at room temperature, and a deoxygenated ethanolic solution (13 mL) of 1,4,7-triazacyclononane (1 M) was added. A light yellow precipitate of $[Co(tacn)_2]Cl_2$ formed immediately and was filtered off and dried under an argon atmosphere. Single crystals of the iodide salt were grown from a deoxygenated, saturated aqueous solution of the chloride salt to which a small quantity of hydrazine had been added to ensure a reducing environment. Upon addition of a saturated aqueous solution of NaI and cooling to 0 °C, light yellowish crystals of X-ray quality formed.

$[((S)\text{-Metacn})Co(tacn)]Cl_3 \cdot 5H_2O$. $[((S)\text{-Metacn})Co(tacn)]Cl_3 \cdot 5H_2O$ has been synthesized analogously to the case of $[((R)\text{-Metacn})Co(tacn)]Cl_3 \cdot 5H_2O$.[16]

$[Co(ttcn)_2](ClO_4)_3$. To a solution of $[Co(ttcn)_2](ClO_4)_2$[17b] (0.31 g; 0.5 mmol) in water (30 mL) was added a saturated aqueous solution of $Na_2S_2O_8$ (5 mL). An immediate color change from violet to orange was observed. Addition of sodium perchlorate monohydrate (1 g) initiated the precipitation of orange-yellow crystals, which were filtered off, washed with ethanol and ether, and air-dried (yield: 0.33 g; 95%). Anal. Calcd for $C_{12}H_{24}S_6CoCl_3O_{12}$: C, 20.1; H, 3.4; S, 26.8; Co, 8.2. Found: C, 20.2; H, 3.3; S, 26.8; Co, 8.1.

X-ray Structure Determinations. A nearly spherical light yellow crystal of $[Co(tacn)_2]I_2 \cdot 2H_2O$ and an orange crystal of $[Co(ttcn)_2](ClO_4)_3$ were each attached to the end of a glass fiber and mounted on an AED II Siemens diffractometer. Preliminary examinations showed that the former crystal belonged to the orthorhombic system, space group *Ibca* (D_{2h}^{27}) whereas the latter belonged to the monoclinic system, space group *C*2/*c* (C_{2h}^{6}). The unit cell dimensions (22 °C) were obtained by least-squares fit of the setting angles of 32 reflections, respectively. The data are summarized in Table I. Intensity data were measured at 22 °C by ω-scans and were corrected for Lorentz and polarization effects

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Table III. Selected Bond Distances (Å) and Angles (deg) of the $Co^{II}N_6$ Skeleton in $[Co(tacn)_2]I_2{\cdot}2H_2O$

Co–N1	2.124 (13)	Co–N3	2.152 (16)
Co–N2	2.190 (14)		
N1–Co–N1′	97.4 (8)	N1–Co–N2	176.9 (9)
N1–Co–N3′	80.9 (7)	N2–Co–N3′	95.9 (8)
N1′–Co–N3′	99.6 (8)	N2–Co–N2′	98.5 (8)
N2–Co–N3	95.6 (8)	N2′–Co–N3′	83.7 (7)
N1–Co–N2′	82.1 (7)	N3–Co–N3′	180.0

Table IV. Atomic Coordinates ($\times 10^4$) of $[Co(ttcn)_2](ClO_4)_3$

atom	*x*	*y*	*z*
Co	2500	2500	5000
S1	3523.7 (7)	2358.5 (6)	6484.1 (6)
S2	1762.0 (7)	1152.8 (6)	5184.3 (6)
S3	3866.9 (7)	1864.7 (6)	4241.7 (6)
Cl1	0	330.5 (8)	2500
Cl2	1693.1 (8)	6124.6 (6)	5396.2 (7)
C1	3504 (3)	1165 (2)	6655 (3)
C2	2360 (3)	783 (2)	6411 (3)
C3	4704 (3)	2790 (2)	3894 (3)
C4	3157 (3)	1539 (3)	3055 (2)
C5	2619 (3)	2758 (3)	7407 (3)
C6	354 (3)	1447 (3)	5393 (2)
O11	0	−610 (3)	2500
O12	804 (10)	763 (7)	1963 (10)
O13	5966 (8)	5485 (6)	3230 (7)
O14	6061 (107)	5686 (8)	2688 (11)
O15	5133 (16)	5735 (10)	3396 (11)
O16	5816 (30)	4620 (27)	3137 (25)
O17	4475 (9)	5593 (6)	3461 (7)
O21	990 (2)	6772 (2)	5785 (2)
O22	2793 (3)	6265 (3)	5815 (3)
O23	1611 (4)	6184 (3)	4342 (2)
O24	1354 (4)	5271 (3)	5669 (3)

in the usual manner. Empirical absorption corrections have been carried out in both cases.[18] The structures were solved via Patterson and Fourier syntheses. Idealized positions of the methylene H atoms were calculated on the basis of d(C–H) of 0.96 Å and sp^3-hybridized C atoms and included in the refinement cycles with isotropic thermal parameters (supplementary material). The function minimized during least-squares refinements was $\sum w(|F_o| - |F_c|)^2$ with final convergence factors $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ where $w = 1/\sigma^2(F)$ (Table I). Scattering factors for all atoms were taken from ref 19. The real and imaginary parts of anomalous dispersion for all non-hydrogen atoms are included.[19]

The quality of the crystal of $[Co(tacn)_2]I_2{\cdot}2H_2O$ used was not very high. The I, Co, and N atoms were refined with anisotropic thermal parameters; the C atoms of the cyclic amine were refined with isotropic thermal parameters only.

In $[Co(ttcn)_2](ClO_4)_3$ one of the perchlorate anions was found to be disordered (Cl1). A model, in which Cl1 and O11 had occupancy factors of 0.5 (both atoms lying on a crystallographic twofold axis) and six different locations of the three remaining oxygen atoms of this ClO_4^- group with an occupancy of 0.25, was satisfactorily refined with isotropic thermal parameters for the O atoms of this disordered ClO_4^- group. All other non-hydrogen atoms were refined with anisotropic thermal parameters. Final difference Fourier syntheses of both structures were essentially featureless. The final atomic parameters of $[Co(tacn)_2]I_2{\cdot}2H_2O$ are given in Table II, those of $[Co(ttcn)_2](ClO_4)_3$, in Table IV. Selected bond distances and angles are summarized in Table III for $[Co(tacn)_2]I_2{\cdot}2H_2O$ and in Table V for $[Co(ttcn)_2](ClO_4)_3$. Listings of observed and calculated structure factors, anisotropic and isotropic thermal parameters, and calculated positional parameters of hydrogen atoms are available as supplementary material.

Electrochemistry. The apparatus used for cyclic voltammetric measurements has been described previously.[20] Cyclic voltammograms of $[((R)\text{-Metacn})Co(tacn)]Cl_3{\cdot}5H_2O$ and $[((S)\text{-Metacn})Co(tacn)]Cl_3{\cdot}5H_2O$ were measured in aqueous solution with 0.1 M KCl as supporting electrolyte at a hanging-mercury-drop electrode at 25 °C. The concentration of the respective sample was 7.2×10^{-4} M. Measurements were made under an argon atmtosphere with an Ag/AgCl reference electrode. The cyclic voltammogram of $[Co(ttcn)_2](ClO_4)_3$ was recorded in aqueous solution with 0.1 M NaCl as supporting electrolyte at a gold electrode under otherwise identical conditions. Cyclic voltammograms were recorded at scan rates 20–200 mV s^{-1}. Formal redox potentials are given vs. the normal hydrogen electrode in volts. The AgCl/Ag electrode had a potential of 0.200 V vs. NHE.

Table V. Selected Bond Distances (Å) and Angles (deg) in $[Co(ttcn)_2](ClO_4)_3$

Co–S1	2.258 (1)	S2–C6	1.820 (4)
Co–S2	2.253 (1)	S3–C3	1.820 (4)
Co–S3	2.249 (1)	S3–C4	1.808 (3)
S1–C1	1.823 (4)	C1–C2	1.517 (5)
S1–C5	1.836 (4)	C3–C6	1.507 (5)
S2–C2	1.824 (4)	C4–C5	1.517 (5)
S1–Co–S1′	180.0	S1–Co–S2	90.6 (1)
S1–Co–S3′	90.8 (1)	S1′–Co–S2	89.4 (1)
S1′–Co–S3′	89.3 (1)	S2′–Co–S3′	89.0 (1)
S2′–Co–S3	91.0 (1)	S1–Co–S2′	89.4 (1)

Magnetic Measurements. The magnetic susceptibility of a powdered sample of $[Co(tacn)_2]I_2{\cdot}2H_2O$ was measured by using the Faraday method (Sartorius microbalance, Bruker research magnet B-E 100C88 and Bruker B-VT 1000 automatic temperature control) between 100 and 298 K, and diamagnetic corrections were applied with use of Pascal's constants.[21]

Kinetic Measurements. Standard syringe techniques were used for reactions with $[Cr(OH_2)_6]^{2+}$ and $[V(OH_2)_6]^{2+}$ with use of argon blanketing gas. The kinetics of the reductions of $[Co(tacn)_2]^{3+}$ with these reductants were followed on a UNICAM SP 1700 spectrophotometer interfaced to a Commodore VC 64 computer for data acquisition and analysis. All reactions were run under pseudo-first-order conditions with the respective reductant in excess over $[Co^{III}]$; $[H^+] = 0.1$ M, and $I = 1.0$ M ($LiClO_4$). The reactions were monitored at $\lambda = 460$ nm. The reductants were prepared electrolytically from perchloric acid solutions of $[Cr(OH_2)_6]^{3+}$ and $[VO(OH_2)_5]^{2+}$, respectively. Pseudo-first-order rate constants were calculated by using a least-squares program[22] where the absorptions at the beginning ($t = 0$) and after the completed reaction ($t = \infty$) were treated as variables.

The kinetics of the reaction between $[Co(ttcn)_2]^{3+}$ and $[Co(phen)_3]^{2+}$ were measured spectrophotometrically with a stopped-flow spectrophotometer interfaced to a Commodore VC 64 computer for data acquisition and analysis at $\lambda = 476$ nm. The ionic strength was adjusted to 0.2 M with NaCl as supporting electrolyte. Pseudo-first-order rate constants (excess $[Co(phen)_3]^{2+}$) were calculated as described above.

The kinetics of the electron-exchange reaction between $[((R)\text{-Metacn})Co(tacn)]^{2+}$ and $[((S)\text{-Metacn})Co(tacn)]^{3+}$ were measured by following the change in circular dichroism of solutions containing both species as a function of time. Solutions of $[((R)\text{-Metacn})Co(tacn)]^{2+}$ in 0.1 M $LiClO_4$ were made in situ by reducing solutions of $[((R)\text{-Metacn})Co(tacn)]Cl_3{\cdot}5H_2O$ with zinc amalgam under an argon atmosphere. The concentrations of the Co(II) solutions were calculated from the concentration of the starting material. Solutions containing the Co(III) and Co(II) species respectively were transferred to two compartments of a tandem mixing cell (Hellma), and mixing of the two solutions was achieved by vigorous shaking of the cell for 10 s.

Electronic Spectra. Electronic spectra of cobalt complexes were measured in aqueous solution on a Perkin-Elmer Lamba 9 spectrophotometer. CD spectra of $[((S)\text{-Metacn})Co(tacn)]Cl_3{\cdot}5H_2O$ and of $[((R)\text{-Metacn})Co(tacn)]Cl_3{\cdot}5H_2O$ and their reduced Co(II) analogues were recorded in aqueous solution on a Dichrograph Mark III instrument (Jobin Yvon).

^{1}H NMR Spectra. ^{1}H NMR spectra of $[(Co(tacn)_2]^{3+}$ and $[Co(ttcn)_2]^{3+}$ were recorded in D_2O solution on a Bruker AM 400 spectrometer (^{1}H NMR frequency 400.13 MHz) with Me_4Si as external standard.

Results

Syntheses, Spectra, and Magnetism of Complexes. The cobalt complexes $[Co(tacn)_2]Br_3{\cdot}5H_2O$, $[Co(tacn)_2]Cl_2$, $[((R)\text{-Metacn})Co(tacn)]Cl_3{\cdot}5H_2O$, and $[Co(ttcn)_2](ClO_4)_2$ have been

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(18) Computations were carried out on an Eclipse computer using the program package STRUCSY (Structure Computation System; Stoe: Darmstadt, FRG).

(19) *International Tables of X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(20) Wieghardt, K.; Bossek, U.; Chaudhuri, P.; Herrmann, W.; Menke, B. C.; Weiss, J. *Inorg. Chem.* **1982**, *21*, 4308.

(21) Earnshaw, A. *Introduction to Magnetochemistry*; Academic: New York, 1968.

(22) DeTar, D. F. *Comput. Chem.* **1978**, *2*, 99.

Table VI. Electronic Spectra, Redox Potentials, and Magnetic Moments of Complexes

complex	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})	$E_{1/2}$,[d] V (vs. NHE)	μ_{eff}(293 K), μ_B	ref
$[Co(tacn)_2]^{3+}$	458 (100), 333 (89)	−0.41[a] (reversible)	diamagnetic	3, 6
$[Co(tacn)_2]^{2+}$	850 (2.4), 630 (1.4), 545 sh, 462 (5.9), 318 sh		5, 18	6
$[Co((R)\text{-Metacn})(tacn)]^{3+}$	463 (86), 333 (76)	−0.41 (reversible)	diamagnetic	16
$[Co((R)\text{-Metacn})(tacn)]^{2+}$	463 (11), 333 (8.2)		not measured	this work
$[Co((S)\text{-Metacn})(tacn)]^{3+}$	463 (83), 333 (75)	−0.41 (reversible)	diamagnetic	this work
$[Co(ttcn)_2]^{3+}$	476 (320), 330 (22000)	+0.42 (quasi-reversible),[c] −0.48 (quasi-reversible)[e]	diamagnetic	this work
$[Co(ttcn)_2]^{2+}$	730 (11), 560 sh, 480 (92), 338 (6600), 264 (6500)[b]		1.82	17

[a] 0.1 M $LiClO_4$ supporting electrolyte, HMD electrode. [b] In acetonitrile. [c] 0.1 M NaCl supporting electrolyte, gold electrode. [d] Formal redox potentials for the respective $Co^{3+/2+}$ couple. [e] Formal redox potential for the couple $Co^{2+/+}$.

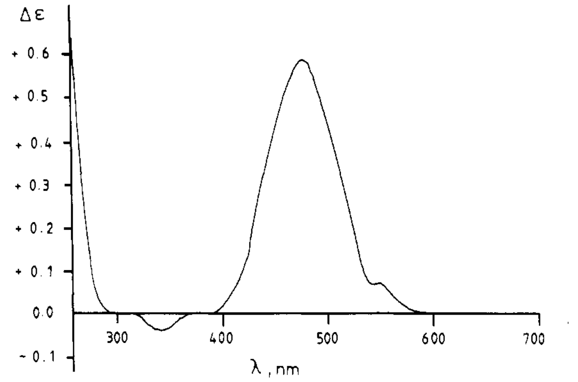

Figure 1. Circular dichroism spectrum of $[((R)\text{-Metacn})Co(tacn)]^{2+}$ in H_2O at 22 °C.

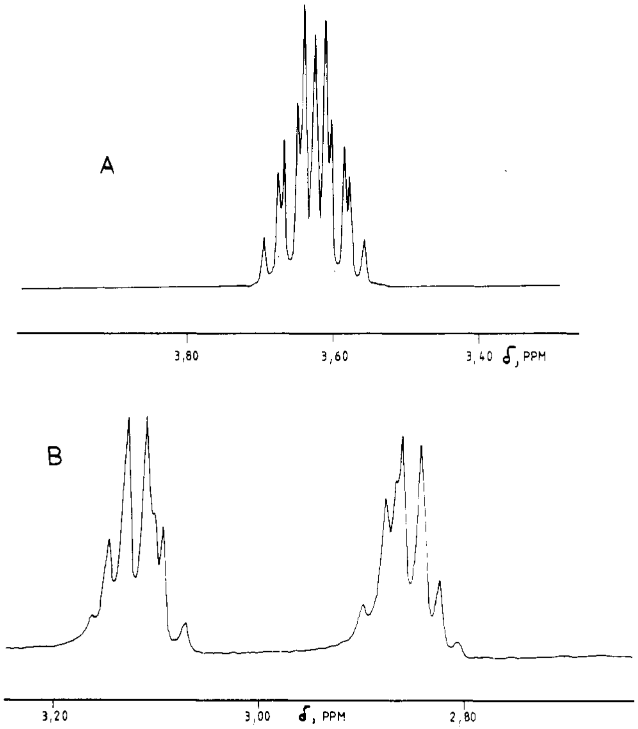

Figure 2. ^1H NMR spectra of (A) $[Co(ttcn)_2]^{3+}$ and (B) $[Co(tacn)_2]^{3+}$ in D_2O solution (22 °C).

prepared previously, and their electronic spectra (Table VI) have been reported. $[Co(tacn)_2]I_2{\cdot}2H_2O$ has been prepared as light yellow crystals of X-ray quality from a deoxygenated aqueous solution of $[Co(tacn)_2]Cl_2$ and sodium iodide. $[((S)\text{-Metacn})Co(tacn)]Cl_3{\cdot}5H_2O$ was synthesized for the first time by reaction of $Co(tacn)Cl_3$ with (*S*)-2-methyl-1,4,7-triazacyclononane in refluxing isopropanol and was recrystallized from water after Sephadex column chromatography.

$[Co(ttcn)_2](ClO_4)_3$ was prepared from an aqueous solution of $[Co(ttcn)_2](ClO_4)_2$ to which $Na_2S_2O_8$ was added as strong oxidant. Orange-yellow crystals of X-ray quality were grown from an aqueous solution of this complex and sodium perchlorate. The electronic spectrum shows a d–d transition at 476 nm (ϵ = 320 L mol^{-1} cm^{-1}), which is assigned $^1A_{1g} \rightarrow {}^1T_{1g}$, and a second band at 330 nm ($\epsilon = 2.2 \times 10^4$), which obviously is due to a ligand-to-metal charge transfer. Details of the electronic spectra, redox potentials, and magnetic properties of all complexes are summarized in Table VI.

The circular dichroism (CD) spectrum of $[((R)\text{-Metacn})Co(tacn)]^{3+}$ was in reasonable agreement with that reported by Nonoyama and Sakai,[16] but in our hands the $\Delta\epsilon$ values were lower by 25% ($\Delta\epsilon_{474} = +3.12$; $\Delta\epsilon_{219} = +7.8$). The CD spectrum of $[((S)\text{-Metacn})Co(tacn)]Cl_3{\cdot}5H_2O$ measured in aqueous solution showed maxima at $\Delta\epsilon_{475} = -3.01$ and $\Delta\epsilon_{214} = -8.6$. The reduced form of $[((R)\text{-Metacn})Co(tacn)]^{3+}$ showed at 475 nm a much weaker Cotton effect ($\Delta\epsilon_{475} = -0.64$). Therefore, the rate of racemization (see below) was followed at 475 nm as a function of time. The CD spectrum of $[((R)\text{-Metacn})Co(tacn)]^{2+}$ is shown in Figure 1. Its enantiomer exhibits a CD spectrum that is the mirror image of this spectrum.

The magnetic susceptibility of $[Co(tacn)_2]I_2{\cdot}2H_2O$ has been measured by the Faraday method between 100 and 298 K and was found to adhere closely to the Curie–Weiss law (μ = 5.08 μ_B; Θ = +14.7 K). This is in good agreement with other high-spin Co(II) complexes in an octahedral environment.[23] Interestingly, the corresponding $[Co(ttcn)_2]^{2+}$ complex is low spin,[17b] indicating an increased ligand field strength of ttcn as compared to its nitrogen-containing analogue tacn.

Figure 2 gives the ^1H NMR spectra in D_2O of $[Co(tacn)_2]^{3+}$ and $[Co(ttcn)_2]^{3+}$, respectively. Both ^1H NMR spectra display a complicated multiplet of the methylene protons. The spectrum of $[Co(tacn)_2]^{3+}$ displays a splitting of this multiplet into two groups of signals, which are symmetrical with respect to each others (δ_1 2.80–2.90 and δ_2 3.06–3.16) and correspond to 12 protons in equatorial positions and 12 protons in axial positions with respect to the two planes of the coordinated 1,4,7-triazacyclononane ligands. These two groups of protons are magnetically inequivalent because they are differently oriented toward the Co(III) center, which leads to a small difference of respective chemical shifts of 0.26 ppm. For $[Co(ttcn)_2]^{3+}$, this difference is much smaller and no splitting is observed. This is thought to be due to the fact that the significantly larger sulfur atoms in the 1,4,7-trithiacyclononane ring as compared to its nitrogen analogue diminish the magnetic inequivalence of axial and equatorial ring protons.

Electrochemistry. Cyclic voltammograms of the enantiomers $[((R)\text{-Metacn})Co(tacn)]^{3+}$ and $[((S)\text{-Metacn})Co(tacn)]^{3+}$ (7.2×10^{-4} M) in 0.1 M KCl exhibit one wave in the potential range +0.2 to −0.8 V vs. NHE, respectively, at a mercury-drop electrode. The peak-to-peak separation of 57 mV and an i_{pa}/i_{pc} ratio of 1.02 ±0.05 indicated in both cases the electrochemical reversibility for the respective one-electron redox process. The formal redox potential (Table VI) was −0.41 V vs. NHE for both enantiomeric couples. The same value has been determined previously for the

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[23] Figgis, B. N.; Lewis, J. *Prog. Inorg. Chem.* **1964**, *6*, 37.

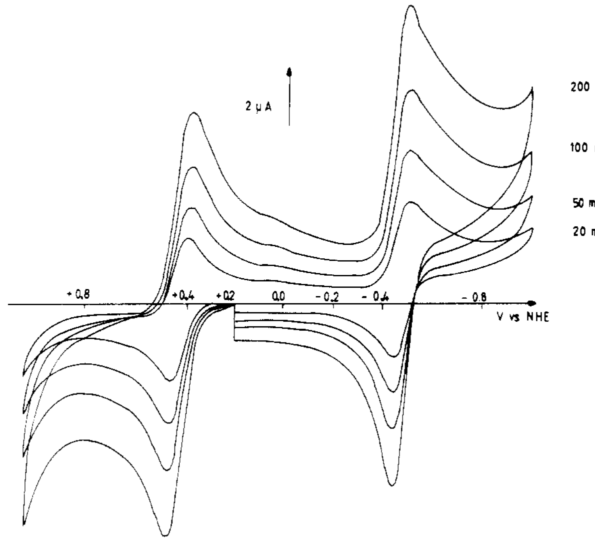

Figure 3. Cyclic voltammogram of $[Co(ttcn)_2](ClO_4)_3$ (0.1 M NaCl supporting electrolyte; gold electrode; 22 °C).

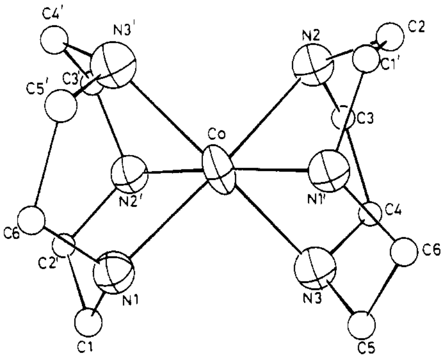

Figure 4. Perspective view and atomic labeling scheme of the cation $[Co(tacn)_2]^{2+}$.

$[Co(tacn)_2]^{3+/2+}$ couple.[3] Thus, the methyl group attached to one carbon atom of one 1,4,7-triazacyclononane ligand in [Co(Metacn)(tacn)]$^{3+}$ complexes does not affect the inherent redox potential of the cobalt centers.

The cyclic voltammogram of $[Co(ttcn)_2]^{3+}$ (10^{-3} M) in aqueous 0.1 M NaCl exhibited two quasi-reversible one-electron couples in the potential range 1.0 to −1.0 V vs. NHE at a gold electrode (Figure 3) at formal redox porentials of +0.42 and −0.48 V vs. NHE. The former potential is assigned to the couple $[Co(ttcn)_2]^{3+/2+}$, whereas the latter corresponds to the couple $[Co(ttcn)_2]^{2+/+}$. Very similar behavior has been reported for the same system in acetonitrile.[17b] Sargeson's CoN_3S_3 macrobicyclic complex exhibits similar electrochemistry (E_1 = ~0 V; E_2 = −1 V).[48] The redox potentials of the couples $[Co(tacn)_2]^{3+/2+}$ and $[Co(ttcn)_2]^{3+/2+}$ are vastly different [$\Delta E_{1/2}$ = 830 mV); the ligand tacn stabilizes the +III oxidation state of cobalt, whereas its sulfur analogue stabilizes cobalt(II).

Description of the Crystal Structures. Crystals of $[Co(tacn)_2]I_2 \cdot 2H_2O$ consist of all the well-separated cations $[Co(tacn)_2]^{2+}$, iodide anions, and water of crystallization. A perspective view of the complex cation and the atomic labeling scheme are shown in Figure 4. The cobalt(II) center lies on a crystallographic twofold axis (C_2 symmetry of the cation). The conformation of the six five-membered $\overline{\text{Co–N–C–C–N}}$ rings within one cation, which are formed by two 1,4,7-triazacyclononane ligands, is either ($\delta\delta\delta$)($\delta\delta\delta$) or ($\lambda\lambda\lambda$)($\lambda\lambda\lambda$), both of which are in the unit cell. No ($\delta\delta\delta$)($\lambda\lambda\lambda$) species are present.

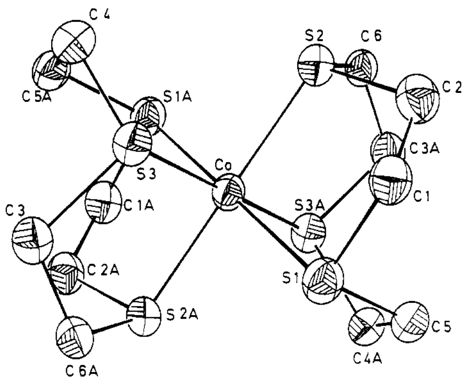

Figure 5. Perspective view and atomic labeling scheme of the cation $[Co(ttcn)_2]^{3+}$.

The six nitrogen atoms form a distorted octahedron about the Co(II) center. The six Co–N bonds form three sets, two of which comprise two nitrogen atoms in cis positions with respect to each other: Co–N1 and Co–N1′ at 2.124 (13) Å; Co–N2 and C–N2′ at 2.190 (14) Å. Co–N3 and Co–N3′ at 2.152 (16) Å are trans with respect to each other. The average C–N bond distance is 2.155 Å.

Due to steric constraints of the nine-membered rings of the ligand, the respective N–Co–N bond angles of cis nitrogen atoms of one ligand are smaller than 90° (average 82.2°) and a trigonal distortion of the CoN_6 polyhedron is enforced.

It is of interest to compare the present structure with that of $[Co((R)\text{-Metacn})_2]I_3 \cdot 5H_2O$.[24] The average Co–N distance is 1.974 Å, and the average N–Co–N bond angle within one coordinated ligand is 85°. Thus, a difference of 0.18 Å in Co–N bond lengths between the divalent and trivalent form is observed. This difference is to be compared with a Δ(Co–N) value of 0.25 Å found for the couple $[Co(NH_3)_6]^{3+/2+}$, which is significantly larger.[25] The population of e_g^* antibonding orbitals in these high-spin cobalt(II) complexes ($t_{2g}^5e_g^2$) leads to a pronounced lengthening of the Co–N bonds as compared to those of their low-spin cobalt(III) counterparts. The same effect has been demonstrated for the pairs $[Co(sep)]^{3+/2+}$,[26] $[Co(en)_3]^{3+/2+}$[10,27] (sep being Sargeson's cage ligand sepulchrate, en being ethylenediamine), $[Co(bpy)_3]^{3+/2+}$,[10] and $[Co(phen)_3]^{3+/2+}$,[10] where Δ(Co–N) values of 0.17, 0.19, 0.19, and 0.19 Å have been observed.

It has been pointed out by Hancock et al.[28] that the Co–N bond distances in $[Co(tacn)_2]^{3+}$ are somewhat larger than one might expect for a small Co(III) low-spin center coordinated to a secondary amine due to intramolecular repulsion of the two 1,4,7-triazacyclononane rings via nonbonded H···H interactions. This may account for the observed relatively small difference Δ(Co–N) of 0.18 Å for the reduced and oxidized forms.

Crystals of $[Co(ttcn)_2](ClO_4)_3$ consist of the well-separated cations $[Co(ttcn)_2]^{3+}$ and perchlorate anions. Figure 5 shows the complex cation and the atomic labeling scheme. The cobalt(III) center lies on a crystallographic center of symmetry, which leads to ($\delta\delta\delta$)($\lambda\lambda\lambda$) conformations of the five-membered $\overline{\text{Co–S–C–C–S}}$ rings in each complex cation.

The cobalt(III) ions are in a nearly regular octahedral environment of six sulfur atoms. The average Co–S bond distance

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(24) Mikami, W.; Kuroda, R.; Konno, M.; Saito, Y. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 1485.

(25) The difference of Co–N bond distances in the cations $[Co(NH_3)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}$ has been deduced from crystallographic data on the solids $[Co(NH_3)_6]Cl_2$ and a variety of $[Co(NH_3)_6]X_3$ salts to be 0.18 Å[25a] and more recently from EXAFS measurements of these cations in solution to be 0.22 Å.[10] Recently, high-precision X-ray structure determinations on $[Co(NH_3)_6](PF_6)_2$ and $[Co(NH_3)_6](BF_4)_2$[25b] have shown the Co^{II}–N distance to be 2.183 (2) Å, which leads to an even larger Δ(Co–N) value of 0.25 Å. (a) Kime, N. E.; Ibers, J. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 168. (b) Kummer, S.; Babel, D. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1118.

(26) Creaser, I. I.; Geue, R. J.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016.

(27) Wheeler, A.; Brouty, C.; Spinat, P.; Herpin, P. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 2069. Nakatzu, K.; Saito, Y.; Kuraya, H. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 428.

(28) Thöm, V. J.; Boeyens, J. C. A.; McDougall, G. J.; Hancock, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3198.

Table VII. Rate Constants for Electron Transfer between $[((R)\text{-Metacn})Co(tacn)]^{2+}$ and $[((S)\text{-Metacn})Co(tacn)]^{3+}$ (I = 0.1 M ($LiClO_4$))

T, °C	$10^3[Co]_{total}$, M	$[Co^{II}]/[Co^{III}]$	10^4k_{obsd}, s^{-1}	k_{ex}, M^{-1} s^{-1}
22	1.46	1	1.67	0.114
22	1.07	1	1.56	0.146
22	1.14	0.75	1.67	0.146
22	1.14	1.1	1.67	0.146
22	1.97	1.03	2.22	0.114
22	1.03	1.55	1.57	0.15
22	0.88	0.96	1.11	0.13
25	1.39	1.0	2.8	0.20
25	1.00	0.5	1.9	0.19
25	1.00	1.5	1.9	0.19

Table VIII. Kinetic Data of the Reductions of $[Co(tacn)_2]^{3+}$ by $[Cr(OH_2)_6]^{2+}$ and $[V(OH_2)_6]^{2+}$

(A) Reductant: $[Cr(OH_2)_6]^{2+}$ ($[Co^{III}] = 10^{-4}$ M; $[H^+]$ = 0.1 M; I = 1.0 M ($LiClO_4$))

T, °C	$[Cr^{2+}]$, M	10^6k_{obsd}, s^{-1}	10^5k_{Cr}, M^{-1} s^{-1}
25	0.13	5.2	3.76
	0.077	3.2	
	0.045	1.58	
	0.12[a]	3.92	
40	0.117	15.3	11.8
	0.074	7.8	
48.5	0.074	13.7	25.0
	0.137	34.1	
	0.1[b]	25.1	

$\Delta H^* = 14.6 \pm 0.8$ kcal mol^{-1} $\Delta S^* = -30 \pm 3$ cal mol^{-1} K^{-1}

(B) Reductant: $[V(OH_2)_6]^{2+}$ ($[Co^{III}] = 5 \times 10^{-4}$ M; $[H^+]$ = 0.1 M; I = 1.0 M ($LiClO_4$))

T, °C	$[V^{2+}]$, M	10^5k_{obsd}, s^{-1}	10^4k_V, M^{-1} s^{-1}
25	0.096	10.9	11.7
	0.053	6.45	
	0.026	3.05	
33.2	0.045[b]	10.2	23.5
	0.022	5.3	
	0.054	12.5	
	0.0085	2.0	
40.4	0.006	25.4	41.1
	0.009	3.7	
	0.018	7.4	
	0.046	19.4	

$\Delta H^* = 14.6 \pm 0.2$ kcal mol^{-1} $\Delta S^* = -23 \pm 1$ cal mol^{-1} K^{-1}

[a] $[Co^{III}] = 10^{-3}$ M. [b] $[H^+]$ = 0.5 M.

Table IX. Kinetic Data of the Reaction of $[Co(ttcn)_2]^{3+}$ with $[Co(phen)_3]^{2+}$ [a]

T, °C	$10^3[Co(phen)_3{}^{2+}]$, M	k_{obsd}, s^{-1}	k,[b] M^{-1} s^{-1}
16	2.5	2.6	974
	7.5	7.4	
	10.0	9.8	
20	2.5	2.9	1200
	7.5	8.9	
25	2.5	3.1	
	5.0	7.3	1270
	7.5	10.2	
	10.0	13.2	
	12.5	15.7	
35	2.5	4.8	1820
	5.0	10.4	
	10.0	18.2	

[a] $[Co(ttcn)_2{}^{3+}] = 5.1 \times 10^{-4}$ M; I = 0.2 M (NaCl). [b] $\Delta H^* = 5.3 \pm 0.3$ kcal mol^{-1}; $\Delta S^* = -26.5 \pm 1.1$ cal K^{-1} mol^{-1}.

is 2.253 Å. The corresponding reduced form $[Co(ttcn)_2]^{2+}$ is low spin ($t_{2g}{}^6e_g{}^1$),[17b] and the average Co–S distance is 2.321 Å.[17a] The population of the e_g* antibonding orbital in $[Co(ttcn)_2]^{2+}$ by one electron leads to only a moderate increase in the Co–S bond distances (Δ(Co–S) = 0.068 Å). Two effects may account for this observation: (i) the Co^{II}–S bonds are shorter due to π back-bonding; (ii) the Co^{III}–S bonds may be somewhat elongated due to intraligand S···S repulsions, which would be enhanced by coordination to the smaller Co(III) ion as compared to the case of the larger Co(II) ion.

Electron-Transfer Reactions. The kinetic inertness and optical stability of $[((R)\text{-Metacn})Co(tacn)]^{3+/2+}$ and $[((S)\text{-Metacn})Co(tacn)]^{3+/2+}$ in deoxygenated aqueous solution allow the direct determination of the outer-sphere electron-transfer rate constant between the oxidized and reduced forms with use of the method described by Dwyer and Gyarfas.[29] The electron-exchange rate constant was determined in mixing a chiral form of one oxidation state with the catoptric form of the other in equimolar amounts and measuring the change in circular dichroism as a function of time. If electron transfer occurs between the two ions, then the mixture racemizes, and when

$$[((R)\text{-Metacn})Co(tacn)]^{2+} + [((S)\text{-Metacn})Co(tacn)]^{3+} \overset{k_{ex}}{\rightleftharpoons} [((R)\text{-Metacn})Co(tacn)]^{3+} + [((S)\text{-Metacn})Co(tacn)]^{2+} \quad (1)$$

equilibrium is established, no change of the circular dichroism occurs. The change of the circular dichroism of the mixture of $[((S)\text{-Metacn})Co(tacn)]^{3+}$ and $[((R)\text{-Metacn})Co(tacn)]^{2+}$ was monitored at 473 nm as a function of time. The data (Table VII) obey a rate law of the form

$$-\mathrm{d} \ln [(\Delta\epsilon_t - \Delta\epsilon_\infty)/(\Delta\epsilon_0 - \Delta\epsilon_\infty)]/\mathrm{d}t = k_{ex}[Co]_{total} \quad (2)$$

where $\Delta\epsilon_t$ is $\Delta\epsilon$ at any time, $\Delta\epsilon_\infty$ is $\Delta\epsilon$ at equilibrium, and $\Delta\epsilon_0$ is $\Delta\epsilon$ at the beginning of the experiment. Plots of ln $[(\Delta\epsilon_t - \Delta\epsilon_\infty)/(\Delta\epsilon_0 - \Delta\epsilon_\infty)]$ vs. time were linear for 3–4 half-lives. The self-exchange rate constant at 25 °C (I = 0.1 M ($LiClO_4$)) was found to be 0.19 M^{-1} s^{-1}.

The reductions of $[Co(tacn)_2]^{3+}$ by $[Cr(OH_2)_6]^{2+}$ and $[V(OH_2)_6]^{2+}$ are outer-sphere one-electron-transfer processes, respectively, because the inert $[Co(tacn)_2]^{3+}$ complex has not suitable bridging ligands for an inner-sphere precursor complex formation available.

$$[Co(tacn)_2]^{3+} + [Cr(OH_2)_6]^{2+} \xrightarrow[H^+,\ H_2O]{k_{Cr}} [Co(OH_2)_6]^{2+} + [Cr(OH_2)_6]^{3+} + 2tacnH_3{}^{3+} \quad (3)$$

$$[Co(tacn)_2]^{3+} + [V(OH_2)_6]^{2+} \xrightarrow[H^+,\ H_2O]{k_V} [Co(OH_2)_6]^{2+} + [V(OH_2)_6]^{3+} + 2tacnH_3{}^{3+} \quad (4)$$

The kinetics of reactions 3 and 4 follow a simple second-order rate law, eq 5. Values of second-order rate constants k_{Cr} and

$$\begin{gathered} -\mathrm{d}[Co(III)]/\mathrm{d}t = k_M[Co(tacn)_2{}^{3+}][M^{2+}] \\ M = [V(OH_2)_6]^{2+}, [Cr(OH_2)_6]^{2+} \end{gathered} \quad (5)$$

k_V at 25 °C (I = 1.0 M ($LiClO_4$)) are 3.8×10^{-5} M^{-1} s^{-1} and 1.2×10^{-3} M^{-1} s^{-1} (Table VIII). The ratio k_{Cr}/k_V of 0.032 is also indicative of outer-sphere processes for both reactions.

The kinetics of the outer-sphere one-electron reduction of $[Co(ttcn)_2]^{3+}$ by $[Co(phen)_3]^{2+}$ (eq 6) have been measured at 476 nm (decrease of $[Co(ttcn)_2{}^{3+}]$) by stopped-flow spectrophotometry.

$$[Co(ttcn)_2]^{3+} + [Co(phen)_3]^{2+} \rightarrow [Co(ttcn)_2]^{2+} + [Co(phen)_3]^{3+} \quad (6)$$

Pseudo-first-order conditions with excess $[Co(phen)_3]^{2+}$ and an ionic strength of 0.2 M (NaCl) were used. Kinetic data (Table IX) fit a simple second-order rate law (eq 7). A second-order rate constant of 1.3×10^3 M^{-1} s^{-1} at 25 °C has been determined.

$$-\mathrm{d}[Co(ttcn)_2{}^{3+}]/\mathrm{d}t = k[Co(ttcn)_2{}^{3+}][Co(phen)_3{}^{2+}] \quad (7)$$

Discussion

Metrical information concerning the metal–ligand distances on the reduced and oxidized forms of bis complexes of cobalt containing the macrocyclic ligands 1,4,7-triazacyclonone (and its 2-methyl derivative) and 1,4,7-trithiacyclonone is now available.

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In addition, the formal redox potentials of the respective Co(II/III) couples in aqueous solution are known and their redox reactivity toward some outer-sphere one-electron reagents has been established. Finally, the self-exchange rate constant for the reaction between $[((R)\text{-Metacn})Co(tacn)]^{2+}$ and $[((S)\text{-Metacn})Co(tacn)]^{3+}$ has been directly measured. It is assumed in the following discussion that the same exchange rate conforms with that of the $[Co(tacn)_2]^{3+/2+}$ electron-transfer exchange reaction, because one methyl group attached to a carbon atom of the backbone of the nine-membered ring of one coordinated ligand is not likely to affect the redox reactivity or the thermodynamic properties of the cobalt complexes. The latter point has been proven experimentally (the redox potentials are identical).

This information enables a detailed analysis to be carried out of the factors governing the rates of their respective outer-sphere electron-transfer reactions. Self-exchange rate constants for the couples $[Co(tacn)_2]^{3+/2+}$ and $[Co(ttcn)_2]^{3+/2+}$ may be estimated from the reaction data for reactions 4 and 6, and the overall free energy change, by using the Marcus cross-correlation[30-32]

$$\begin{aligned} k_{12} &= (k_{11}k_{22}K_{12}f_{12})^{1/2} \\ \ln f_{12} &= (\ln K_{12})^2/[4 \ln (k_{11}k_{22}/Z^2)] \end{aligned} \tag{8}$$

k_{11} and k_{22} are rate constants for the individual self-exchange reactions, k_{12} is the cross-reaction constant, and K_{12} is the overall equilibrium constant. It is assumed that the work terms to bring the reactants and products, respectively, together for the self-exchange reactions and cross-reactions are the same. Z is a collision frequency and was set to 10^{11} M^{-1} s^{-1}.

From the measured rate constant for the reaction between $[Co(tacn)_2]^{3+}$ and $[V(OH_2)_6]^{2+}$ at 25 °C and $I = 1.0$ M ($LiClO_4$) of 1.2×10^{-3} M^{-1} s^{-1}, a self-exchange rate constant, k_{22}, for the $[V(OH_2)_6]^{3+/2+}$ couple of 1×10^{-2} M^{-1} s^{-1} (25 °C, $I = 1.0$ M),[33] and formal redox potentials for the couples $[Co(tacn)_2]^{3+/2+}$ and $[V(OH_2)_6]^{3+/2+}$ of –0.41 and –0.255 V (vs. NHE),[34] respectively, a self-exchange rate constant for $[Co(tacn)_2]^{3+/2+}$ of 0.08 M^{-1} s^{-1} (25 °C, $I = 1.0$ M) is calculated. This value is in excellent agreement with the measured value of 0.19 M^{-1} s^{-1} (25 °C, $I = 0.1$ M)[35] for the very similar couple $[Co(Metacn)(tacn)]^{3+/2+}$. The same approach leads to a self-exchange rate constant of 1.3×10^4 M^{-1} s^{-1} (25 °C, $I = 0.2$ M NaCl) for $[Co(ttcn)_2]^{3+/2+}$ from a cross-reaction rate constant of 1.27×10^3 M^{-1} s^{-1} (eq 6), a self-exchange rate constant of 40 M^{-1} s^{-1} (25 °C) for the $[Co(phen)_3]^{3+/2+}$ couple,[38] and redox potentials of +0.42 and +0.39 V (vs. NHE) for the couples $[Co(ttcn)_2]^{3+/2+}$ and $[Co(phen)_3]^{3+/2+}$,[32,34] respectively. Thus, the self-exchange rates of $[Co(ttcn)_2]^{3+/2+}$ and $[Co(tacn)_2]^{3+/2+}$ differ by 5 orders of magnitude. Interestingly, Sargeson et al.[39] have recently reported a similar rapid electron-transfer self-exchange involving low-spin cobalt(II) and cobalt(III) cage complexes with an N_3S_3 donor set. For (8-methyl-1,3,13,16-tetraaza-6,10,19-trithiabicyclo-[6.6.6]eicosane)cobalt(III/II) an electron-self-exchange rate constant of 4.5×10^3 M^{-1} s^{-1} at 25 °C has been determined. The accelerating influence of thioether donor atoms on electron transfer for Co(III) complexes has been observed previously.[40-43] As we will show below, this effect is adequately accounted for by the reduced difference of Co–S distances in the oxidized and reduced forms of thioether cobalt complexes as compared to corresponding Δ(Co–N) values of aza cobalt complexes.

Since the rate of electron exchange in the redox couple $[Co(Metacn)(tacn)]^{3+/2+}$ has been determined experimentally and the structures of both forms of $[Co(tacn)_2]^{3+/2+}$ are known, it is of interest to calculate this rate constant with the Marcus–Sutin model as a further test of its predictive power. This recent semiclassical model describes the exchange rate constant k for an outer-sphere electron transfer (eq 10) as the product of a preequilibrium constant K_0, an effective frequency ν_n, and electronic and nuclear factors κ_{el} and κ_n, respectively.

$$[ML_2]^{3+} + [ML_2]^{2+} \rightleftarrows [ML_2]^{2+} + [ML_2]^{3+} \tag{9}$$

$$k = K_0\nu_n\kappa_{el}\kappa_n \tag{10}$$

The value of the preequilibrium constant depends upon the charges and sizes of reactants; it may be obtained from

$$K_0 = \left(\frac{4\pi N r^2 \delta_r}{1000}\right) \exp\left(-\frac{w(r)}{RT}\right) \tag{11}$$

where the reaction thickness δ_r is ca. 0.8 Å and $w(r)$ is the work required to bring the two reactants to the separation distance r. This work is considered to be predominantly electrostatic for all electron-transfer reactions discussed in this paper, and it is assumed that the reaction occurs at $r = (a_2 + a_3)$, where a_2 and a_3 are the radii of the two reactants. The Debye–Hückel expression allows the calculation of $w(r)$ (eq 12), where z_2 and z_3 are the charges

$$w(r) = \frac{z_2 z_3 e^2}{D_s r(1 + \beta r \mu^{1/2})} \tag{12}$$

on the two reactants, D_s is the static dielectric constant of the medium, and $\beta = (8\pi N e^2/(1000 D_s k T))^{1/2}$.

For exchange reactions the nuclear factor contains both solvent and inner-sphere contributions

$$\kappa_n = \Gamma_\lambda \exp[-(\Delta G^*{}_{out} + \Delta G^*{}_{in})/RT] \tag{13}$$

$$\Delta G^*{}_{out} = \frac{(\Delta e)^2}{4}\left(\frac{1}{2a_2} + \frac{1}{2a_3} - \frac{1}{r}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \tag{14}$$

$$\Delta G_{in}{}^* = \frac{1}{2}\sum f_i[(d°_2 - d°_3)_i/2]^2 \tag{15}$$

where Γ_λ is a nuclear tunneling factor, which is defined in eq 16.

$$\Gamma_\lambda = \left(\frac{\sinh \frac{x}{2}}{x}\right)^{1/2}\left[\exp\left(-\frac{\Delta G^*{}_{in}}{4h\nu_{in}}\right)\right]\left[\left(\tanh \frac{x}{4}\right) - \frac{x}{4}\right] \tag{16}$$

$$x = h\nu_{in}/kT$$

D_{op} is the optical dielectric constant of the medium, $f_i = 2f_2f_3/(f_2$

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(35) When the same calculation is carried out for the reaction between $[Co(tacn)_2]^{3+}$ and $[Cr(OH_2)_6]^{2+}$ using the data $k_{12} = 3.8 \times 10^{-5}$ M^{-1} s^{-1} (25 °C, $I = 1.0$ M), a self-exchange rate constant for the couple $[Cr(OH_2)_6]^{3+/2+}$ of 10^{-5} M^{-1} s^{-1} [36] and redox potentials of –0.41 and –0.415 V vs. NHE for the couples $[Co(tacn)_2]^{3+}/^{2+}$ and $[Cr(OH_2)_6]^{3+/2+}$,[34] respectively, a self-exchange rate constant of 1.4×10^{-4} M^{-1} s^{-1} (25 °C) for the $[Co(tacn)_2]^{3+/2+}$ couple is calculated. This value is 3 orders of magnitude smaller than the measured value of 0.19 M^{-1} s^{-1}, despite the fact that the free energy change of the reaction is negligible, in which instance the Marcus equation (8) normally gives quite reliable estimates of exchange rate constants. On the other hand, with the measured exchange rate constant of $[Co(tacn)_2]^{3+/2+}$ the same approach gives an exchange rate constant for $[Cr(OH_2)_6]^{3+/2+}$ of $\sim 10^{-8}$ M^{-1} s^{-1}. A possible explanation for this discrepancy may be that the exchange mechanism of $[Cr(OH_2)_6]^{3+/2+}$ is not of the simple outer-sphere type.[49] Similar observations have been reported for the couple $[Co(OH_2)_6]^{3+/2+}$ is not of the simple outer-sphere type.[49] Similar observations have been reported for the couple $[Co(OH_2)_6]^{3+/2+}$.[37]

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$+ f_3$) is a reduced force constant for the ith inner-sphere vibration, $d^\circ_2 - d^\circ_3 = \Delta d_0$ is the corresponding difference in the equilibrium bond distances in the two oxidation states, and the summation is over all the intramolecular vibrations. The nuclear frequency factor, ν_n, is defined by eq 17. For water as solvent, $\nu_{out} = 0.9$

$$\nu_n{}^2 = \frac{\nu_{out}{}^2\Delta G^*{}_{out} + \nu_{in}{}^2\Delta G^*{}_{in}}{\Delta G^*{}_{out} + \Delta G^*{}_{in}} \tag{17}$$

$\times 10^{12}$ s^{-1} ($\tilde{\nu}_{out} = 30$ cm^{-1}) ands ν_{in} are metal–ligand stretching frequencies.

The exchange reactions of $[Co(tacn)_2]^{3+/2+}$ and $[Co(ttcn)_2]^{3+/2+}$ are assumed to be adiabatic, and the electronic factor κ_{el} is set to unity.

A critical point in our calculations is the lack of a complete normal-coordinate analysis for $[Co(tacn)_2]^{3+/2+}$ complexes, but the force constants for the oxidized and reduced forms (f_3, f_2) of CoN_6–amine complexes are believed not to vary extensively for different amine complexes.

In the present calculations we have used the following numerical values:[44] $f_3 = 248$ N M^{-1} and $f_2 = 139$ N M^{-1}.[50] The Co–N stretching frequencies are observed at 479 cm^{-1} for $[Co(tacn)_2]^{3+}$ [5] and at 395 cm^{-1} for the reduced form. The following parameters are calculated for $[Co(tacn)_2]^{3+/2+}$ from eq 10–17: $K_0 = 0.03$ M^{-1} ($I = 0.1$ M); $\Delta G^*{}_{in} = 13.3$ kcal mol^{-1}; $\Delta G^*{}_{out} = 5.2$ kcal mol^{-1}; $\Gamma_\lambda = 6$ with $r = 8.6$ Å and $d_2 - d_3 = 0.18$ Å. A self-exchange rate constant of 0.07 M^{-1} s^{-1} is calculated. This is in excellent agreement with the measured value and demonstrates the predictive power of the Marcus–Sutin model.

For the system $[Co(ttcn)_2]^{3+/2+}$ the situation is more complicated due to the lack of reliable force constants of Co–S-containing complexes. Only one normal-coordinate analysis on such a system appears to have been carried out on a cobalt(III) complex with a Co–S bond,[45] and we used that value for f_3 (110 N M^{-1}) and made an educated guess for f_2 (70–90 N M^{-1}). The Co–S stretching frequencies of $[Co(ttcn)_2]^{3+/2+}$ have not been identified in the respective infrared spectrum, but again educated guesses would place these frequencies between 300 and 250 cm^{-1} for the trivalent form and 250–200 cm^{-1} for the divalent form. The calculations for the $[Co(ttcn)_2]^{3+/2+}$ exchange rate constant with these assumptions and $r = 8.6$ Å, $d_2 - d_3 = 0.07$ Å,[51] $\Gamma_\lambda = 1.0$, and $K_0 = 0.06$ M^{-1} ($I = 0.2$ M), where $\Delta G^*{}_{out} = 5.2$ kcal mol^{-1} and $\Delta G^*{}_{in}$ ranges from 0.9 to 1.2 kcal mol^{-1}, yield numerical values 1×10^6–7×10^7 M^{-1} s^{-1} at 25 °C. This is about 2–3 orders of magnitude faster than the value derived from the cross-reaction (6). It should be kept in mind that exchange rate constants derived from the Marcus cross-relation are invariably found to be smaller than the measured values[31] and a true exchange rate of $\sim 10^6$ M^{-1} s^{-1} for the couple $[Co(ttcn)_2]^{3+/2+}$ is not unlikely.

It is noted that the inner-sphere reorganization energy, $\Delta G^*{}_{in}$, for cobalt amine complexes usually exceeds the reorganization energy of the solvent spheres, $\Delta G^*{}_{out}$.[10,47] This holds also for the $[Co(tacn)_2]^{3+/2+}$ complexes. In contrast, in the $[Co(ttcn)_2]^{3+/2+}$ system the inner-sphere reorganization energy is smaller than $\Delta G^*{}_{out}$ and resembles in this respect data reported for $[Co(bpy)_3]^{2+}/^{+}$.[10,46] This decreased inner-sphere reorganization energy is apparently the dominant factor for the enhanced self-exchange rates in cobalt–sulfur complexes.[39]

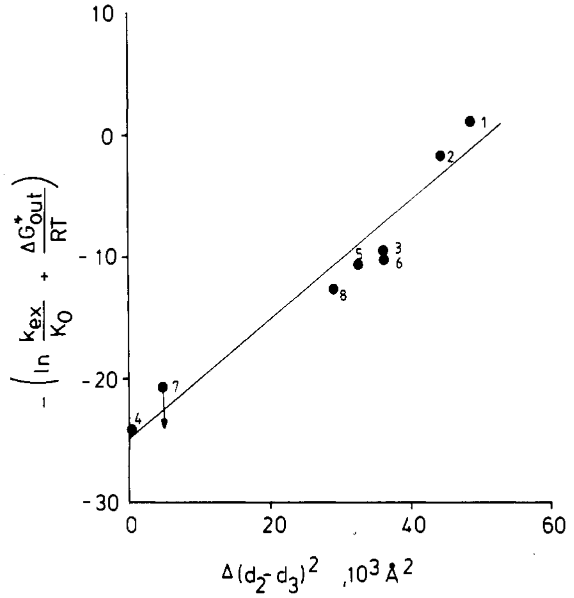

Figure 6. Plot of $-(\ln (k_{22}/K_0) + \Delta G^*{}_{out}/RT)$ vs. $\Delta(d_2 - d_3)^2$ Å^2 for a series of cobalt complexes: 1, $[Co(NH_3)_6]^{3+/2+}$; 2, $[Co(en)_3]^{3+/2+}$; 3, $[Co(bpy)_3]^{3+/2+}$; 4, $[Co(bpy)_3]^{2+/+}$; 5, $[Co(tacn)_2]^{3+/2+}$; 6, $[Co(phen)_3]^{3+/2+}$; 7, $[Co(ttcn)_2]^{3+/2+}$; 8, $[Co(sep)]^{3+/2+}$. Values were taken from ref 10, except those of 5 and 7. For 7, $k_{ex} = 1.4 \times 10^4$ M^{-1} s^{-1}; the arrow indicates a calculated k_{ex} of 10^6 M^{-1} s^{-1} (see text).

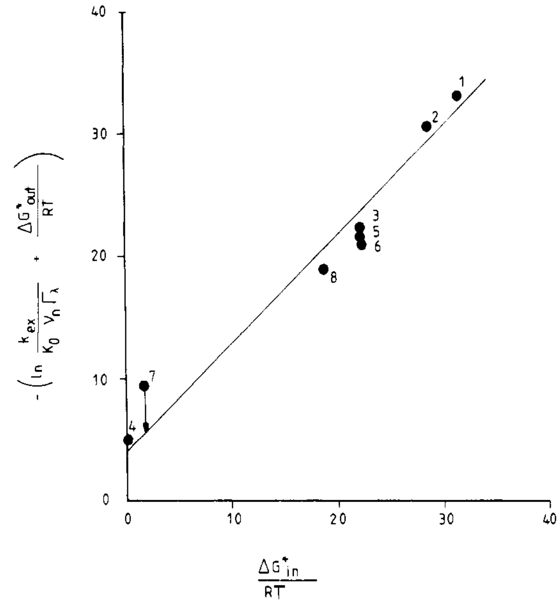

Figure 7. Plot of $-(\ln (k_{22}/K_0\nu_n\Gamma_\lambda) + \Delta G^*{}_{out}/RT)$ vs $\Delta G^*{}_{in}/RT$ for the same series of complexes as in Figure 6.

If the difference of the cobalt to ligand bond distances in the reduced and oxidized forms ($d_2 - d_3$) is the main source for this effect, a plot of the natural logarithm of the observed self-exchange rate constant divided by the precursor formation constant and added outer-sphere reorganization energy divided by RT vs. the square of this bond distance should be linear,[10] neglecting differing force constants and nuclear and electronic factors for the complexes. They are assumed to be constant for the present purpose. Figure 6 shows this plot for a series of cobalt complexes. A reasonably linear dependence is observed. The $[Co(tacn)_2]^{3+/2+}$ and $[Co(ttcn)_2]^{3+/2+}$ systems also fit nicely; a difference of self-exchange rates of 5–6 orders of magnitude is satisfactorily accounted for. If, finally, all the so far neglected factors are included and

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(50) In a more rigorous treatment a full molecular mechanics calculation would have to be carried out in order to estimate the strain energy of the actual bonds. The numbers used here are for the a_{1g} vibrations of $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{2+}$.[44]

(51) The low-spin $[Co(ttcn)_2]^{2+}$ complex is equatorically expanded 0.11 + 0.01 Å and axially compressed 0.01 + 0.005 Å[17a] compared to the case of the $[Co(ttcn)_2]^{3+}$ complex. It is therefore a crude approximation to use the averaged bond lengths in calculating reorganizational barriers to electron transfer, and $\Delta G^*{}_{in}$ may be ca. 50% bigger than estimated here, which would lead to a slower calculated self-exchange rate.

$$-\left(\ln \frac{k_{\mathrm{ex}}}{K_0 \nu_{\mathrm{n}} \Gamma_\lambda} + \frac{\Delta G^*{}_{\mathrm{out}}}{RT}\right) \text{ vs. } \frac{\Delta G^*{}_{\mathrm{in}}}{RT}$$

is plotted (Figure 7), a nice linear dependence is observed. This plot encompasses self-exchange rates of cobalt complexes, which span 11 (!) orders of mangitude.[10]

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Supplementary Material Available: Listings of anisotropic and isotropic thermal parameters, calculated positional parameters of hydrogen atoms, and intraligand bond distances of $[Co(tacn)_2]I_2{\cdot}2H_2O$ and of $[Co(ttcn)_2](ClO_4)_3$, respectively (5 pages). Ordering information is given on any current masthead page.

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Exchange Interaction in Multinuclear Transition-Metal Complexes. 9.[1] Magnetostructural Correlations in One-Atom Acetato-Bridged Copper(II) Dimers

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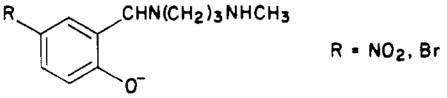
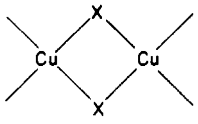
The syntheses, crystal and molecular structures, and magnetic properties are reported for the new complexes $Cu_2(5\text{-}NO_2\text{-}L)_2(CH_3COO)_2$ and $Cu_2(5\text{-}Br\text{-}L)_2(CH_3COO)_2$, where $(5\text{-}NO_2\text{-}L)^-$ and $(5\text{-}Br\text{-}L)^-$ are the anions of *N*-methyl-*N'*-(5-nitrosalicylidene)-1,3-propanediamine and *N*-methyl-*N'*-(5-bromosalicylidene)-1,3-propanediamine, respectively:



The 5-nitro complex, $Cu_2C_{26}H_{34}N_6O_{10}$, crystallizes in the triclinic space group $P\bar{1}$. Cell dimensions: $a = 9.305$ (3), $b = 9.209$ (3), $c = 8.993$ (3) Å; $\alpha = 94.94$ (2), $\beta = 94.92$ (2), $\gamma = 92.78$ (2)°. $Z = 1$. The structure was solved by Patterson and Fourier methods and refined to an R (unweighted) value of 0.026 (R(weighted) = 0.030) for 208 parameters and 2086 observed reflections. The 5-bromo complex, $Cu_2C_{26}H_{34}N_4O_6Br_2$, crystallizes in the monoclinic space group $P2_1/a$. Lattice parameters: $a = 14.519$ (2), $b = 10.859$ (2), $c = 9.547$ (3) Å; $\beta = 93.35$ (2)°. $Z = 2$. The structure was solved by Patterson and Fourier methods. The final R index was 0.045 for 1674 observations and 113 parameters ($R_w = 0.053$). Both complexes consist of centrosymmetric dimeric units that are well separated from one another. The dimeric units are very similar. Each copper atom shows distorted (4 + 1 + 1) square-bipyramidal coordination. The four short bonds, which lie approximately in a plane, are to the two cis nitrogens and the phenolic oxygen of a tridentate Schiff base ligand, and one oxygen atom of an acetate anion. Each complete fragment so formed is linked via a fifth weak bond to the in-plane coordinated acetate oxygen atom of the other. Therefore, each bridging oxygen simultaneously occupies an in-plane coordination site on one copper(II) ion and an apical site of the other copper(II) ion. The second oxygen atom of each acetate ligand is at a weakly linking distance of only one copper atom and is not involved in any bridging. The four-membered Cu_2O_2 bridging units in the dimers are strictly planar owing to crystallographic inversion symmetry. In the 5-nitro complex the bridging angle at oxygen is 96.1 (1)°, and the long, out-of-plane Cu–O bond distance is 2.577 (2) Å, while the corresponding values in the 5-bromo complex are 96.3 (2)° and 2.665 (4) Å, respectively. The magnetic susceptibilities of powdered samples of the complexes have been examined down to ca. 2 K. The two compounds exhibit antiferromagnetic exchange interactions with the best fit to an appropriate dimer-exchange equation yielding singlet–triplet splittings of -3.02 cm^{-1} for the 5-nitro complex and -3.68 cm^{-1} for the 5-bromo complex. A comparison of the structural and magnetic data obtained for the present compounds with corresponding data for five previously characterized compounds that involve similarly bridged Cu_2O_2 moieties shows that a smooth correlation of $2J$ with the ϕ/R_0 quotient, where ϕ is the bridging angle at oxygen and R_0 is the axial Cu–O bond distance, begins to emerge.

Introduction

Dinuclear copper(II) complexes with planar, I, or parallel-planar, II, geometries have occupied considerable experimental[2a,b,d–f] and theoretical[2c,3–5] work.



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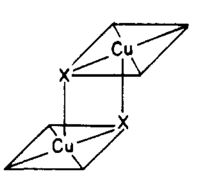

II

Much of this work has been concerned with the correlation of the structural properties of these complexes with their magnetic properties.

For planar hydroxo-bridged systems of type I it has been possible to establish,[2a,6] and theoretically justify,[2c,3] that the sin-

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