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Studies Involving Nitrogen–Oxygen Donor Macrocyclic Ligands. 3. Cobalt(II) Complexes of Cyclic Diimine Ligands Derived from Salicylaldehyde and 5-Chloro-2-hydroxybenzophenone. X-Ray Structure Determination of *cis*-Co(C₁₉H₂₀N₂O₂)(NCS)₂¹

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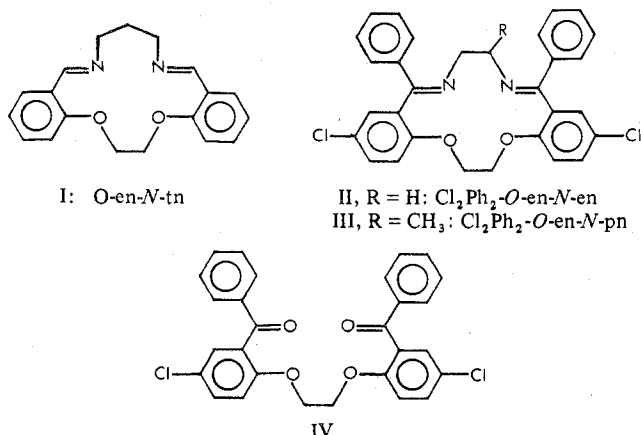
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The interaction of cobalt(II) with three 14- or 15-membered macrocyclic ligands each incorporating two ether oxygen and two imine nitrogen donor atoms has been investigated. A range of cobalt(II) complexes with metal to macrocycle ratios of 1:1 have been isolated and these are either five- or six-coordinate. For one ligand, two isomeric thiocyanate complexes Co(C₁₉H₂₀N₂O₂)(NCS)₂ were isolated—orange and purple forms. Physical measurements indicate that these isomers are *trans*- and *cis*-octahedral forms. The purple isomer crystallizes in the monoclinic space group *P2₁/c* with cell dimensions of *a* = 8.299 (3) Å, *b* = 18.538 (5) Å, *c* = 14.750 (4) Å, and β = 100.90 (5)°. The crystal structure was determined using 1208 four-circle diffractometer data with $I_{\text{obsd}} \geq 3\sigma(I)$ and refined to conventional and weighted residuals of 0.058 and 0.059. In this complex the macrocycle is folded, giving a β -*cis* configuration and, with two N-bonded thiocyanate anions, defines an irregular octahedron of donors about the cobalt(II) ion.

The chemistry of macrocyclic ligands can be divided into two major parts. The first of these incorporate ligands of the "crown" polyether type³. Such ligands generally show high affinity for many alkali metal or alkaline earth ions but coordinate much less strongly to transition metal ions. In contrast, a large number of macrocyclic ligands (both naturally occurring and synthetic) which contain four nitrogen donors are now known⁴ and these are usually excellent complexing agents toward most transition metal ions, but poorer ligands toward many nontransition ions such as those of groups 1A and 2A.

As a continuation of the study of the complexing behavior of ligands which are intermediate structurally between the above two categories^{1,5}, we now report an investigation of the interaction of cobalt(II) with the macrocycles I, II, and III.



The interaction of I with nickel(II), copper(II), and cadmium(II) has been reported previously^{1,5} but the related substituted macrocycles of types II and III have not been previously studied. These latter ligands were obtained by con-

densation of the diketone precursor IV with the corresponding diamine.

Experimental Section

Analyses for carbon, hydrogen, and nitrogen were determined by Mr. J. Kent of the Microanalytical Laboratory, University of Queensland, or by Dr. E. Challen, University of New South Wales. Cobalt was determined by atomic absorption spectroscopy. All compounds were dried over P₂O₁₀ in vacuo before analyses. The various instrumental techniques as well as the synthesis of I, O-en-N-tn, were performed as described previously.¹ We thank Dr. R. Vagg for the mass spectra.

Preparation of IV. This diketone was obtained by means of a Williamson condensation between 5-chloro-2-hydroxybenzophenone and 1,2-dibromoethane as described previously:⁵ yield 40%; mp 164 °C; ¹H NMR δ 3.89 (s, CH₂), 6.6–7.8 (m, aromatic). Anal. Calcd for C₂₈H₂₀Cl₂O₄: C, 68.44; H, 4.10. Found: C, 68.20; H, 4.22.

General Preparation for II or III. The diketone IV and a slight excess of 1,2-diaminoethane or 1,2-diaminopropane were heated together at reflux for 1 h. The residue was dissolved in hot butanol and any insoluble material was filtered off. The solution was then taken to dryness and the crude macrocycle was recrystallized from benzene and ether. The product was dried in vacuo at 120 °C. Anal. Calcd for II, C₃₀H₂₄Cl₂N₂O₂: C, 69.96; H, 4.69; N, 5.43. Found: C, 70.02; H, 4.62; N, 5.55. Calcd for III, C₃₁H₂₆Cl₂N₂O₂: C, 70.32; H, 4.95; N, 5.29. Found: C, 70.17; H, 4.91; N, 5.21.

General Preparation for Complexes of II or III. A hot solution of II or III in benzene was added to a solution of a slight excess of cobalt salt in hot absolute alcohol. This reaction solution was boiled down on a hot plate until precipitation occurred. The product was filtered off from the boiling solution. It was washed with benzene, alcohol, and then petroleum ether.

General Preparation for Complexes of the Type [Co(O-en-N-tn)X](ClO₄)_n·nH₂O (n = 0 or 1). To a warm methanol solution of cobalt(II) perchlorate hexahydrate was added a mixture of O-en-N-tn and excess lithium halide in methanol. The precipitate which formed was filtered and washed with methanol.

Diiodo[5,6:14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadecane-7,12-diene]cobalt(II), Co(O-en-N-tn)₂. Cobalt(II) nitrate hexa-

hydrate, *O-en-N*-tn, and excess lithium iodide in a procedure similar to the above yield a brown precipitate of $\text{Co}(\text{O-en-N-tn})\text{I}_2$.

Dithiocyanato(5,6:14,15-dibenzo-1,4-dioxo-8,12-diazacyclopentadecane-7,12-diene)cobalt(II), $\text{Co}(\text{O-en-N-tn})(\text{NCS})_2$. To cobalt(II) perchlorate hexahydrate (0.36 g, 1 mmol) in methanol (30 cm³) were added *O-en-N*-tn (0.31 g, 1 mmol) and sodium thiocyanate (0.32 g, 4 mmol) in methanol (20 mL). The orange form of $\text{Co}(\text{O-en-N-tn})(\text{NCS})_2$, which precipitated immediately, was filtered off and washed with methanol and then ether. The filtrate yielded the other isomer of $\text{Co}(\text{O-en-N-tn})(\text{NCS})_2$ as purple crystals which were collected and washed as above.

See Table I for analytical and physical data of the complexes.

X-Ray Crystallography

Crystal data: $\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_2\text{S}_2\text{Co}$, mol wt 483.5, monoclinic, $a = 8.299$ (3) Å, $b = 18.538$ (5) Å, $c = 14.750$ (4) Å, $\beta = 100.90$ (5)°, $V = 2228$ Å³, $d_{\text{meas}} = 1.45$ g cm⁻³, $Z = 4$, $d_{\text{calcd}} = 1.441$ g cm⁻³; $\lambda(\text{Mo K}\alpha) 0.7107$ Å, $\mu(\text{Mo K}\alpha) = 9.2$ cm⁻¹.

The space group $P2_1/c$ was assumed from systematic extinctions ($0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$) and subsequently confirmed by satisfactory refinement of the structure.

Data were collected on a crystal with dimensions ca. $0.13 \times 0.10 \times 0.05$ mm using a Philips PW1100 four-circle diffractometer and graphite-monochromatized Mo K α radiation. The ω - 2θ scan mode was used, and reflections with $3.0 < \theta < 25.0^\circ$ in one quadrant were examined. Most intensities were measured more than once: weak reflections which gave $I_{\text{top}} - 2I_{\text{top}}^{1/2} < I_{\text{back}}$ on a preliminary scan were not further examined (I_{top} is the intensity at the top of the reflection peak and I_{back} is the mean of two preliminary 5-s background measurements on either side of the peak). Of the remaining 1450 reflections those for which the total intensity recorded in the first scan of the peak (I_{int}) was < 500 counts were scanned twice to increase their accuracy. A constant scan speed of $0.05^\circ \text{ s}^{-1}$ and a variable scan width of $(0.7 + 0.1 \tan \theta)^\circ$ were used, with a background-measuring time proportional to $I_{\text{back}}/I_{\text{int}}$. Three standard reflections were measured every 3 h during data collection and showed no significant variations in intensity.

The reflection intensities were calculated from the peak and background measurements using a program written for the PW1100 diffractometer.⁶ The variance of the intensity, I , was calculated as the sum of the variance due to counting statistics and $(0.04I)^2$, where the term in I^2 was introduced to allow for other sources of error.⁷ I and $\sigma(I)$ were corrected for Lorentz and polarization factors and reflections for which $I \leq 3\sigma(I)$ were rejected. No absorption corrections were applied. Averaging of multiple measurements or symmetry-equivalent reflections gave 1208 unique reflections.

Structure Solution and Refinement. The cobalt and two sulfur atoms were located from a Patterson map. Least-squares refinement of their positional and isotropic thermal parameters gave $R = 0.366$. A subsequent difference Fourier synthesis revealed the positions of all of the remaining nonhydrogen atoms. Refinement with isotropic thermal parameters for all atoms converged at $R = 0.099$. In the final six cycles of refinement anisotropic thermal parameters were assigned to the cobalt and sulfur atoms only. Hydrogen atoms were included in calculated positions, "riding" at a fixed distance of 1.08 Å from the carbon atoms to which they are attached⁸ and having isotropic thermal parameters 20% greater than those of the attached atoms. This resulted in $R = 0.058$ and $R_w = 0.059$ [where $R_w = \sum |F_o| - |F_c| |w|^{1/2} / \sum |F_o| w^{1/2}$ and weights (w) were assigned to reflections as $w = 1/\sigma^2(F_o)$]; maximum shift = 0.017σ and average shift = 0.028σ . The final difference Fourier map showed maxima and minima of electron density of 0.36 and $-0.33 \text{ e } \text{Å}^{-3}$, respectively.

Major computations were performed using the SHELX programs.⁸ Scattering factors and anomalous dispersion corrections for cobalt were taken from ref 9 and 10.

Atomic positional and thermal parameters are given in Tables II and III. Bond lengths and angles are presented in Tables IV and V. A table of observed and calculated structure factors is available as supplementary material.

Results and Discussion

Cobalt(II) complexes (Table I) of the macrocyclic ligand *O-en-N*-tn (I) were prepared directly in methanol from the free ligand. All complexes give infrared absorptions which confirm the presence of aromatic and imine functions. For the perchlorate complexes, the infrared spectra contain

Table I. Physical Data for Cobalt(II) Macrocyclic Complexes

Compd ^a	% C	% H	% N	% Co	Magnetic moment ^b	Infrared bands, cm ⁻¹		Anion	Molar conductivity ^c	Visible spectral bands, d cm ⁻¹
						Aromatic and imine	Carbonyl			
[Co(O-en-N-tm)Cl]ClO ₄ (pink)	Calcd 45.11	4.01	5.58	11.7	4.79	1650 sh, 1640,	1090		27	17 900, 14 300 sh, 10 000, 8300
	Found 45.41	4.40	5.18	12.0	(296)	1600, 1575 sh				
[Co(O-en-N-tm)Br](ClO ₄)·H ₂ O (purple)	Calcd 40.41	3.92	4.96	10.4	4.90	1635 sh, 1625,	1110,		25	17 900, 14 300 sh, 10 200
	Found 40.46	3.92	4.79	10.7	(298)	1595, 1575 sh	1050			
[Co(O-en-N-tm)](ClO ₄)·H ₂ O (brown)	Calcd 37.31	3.62	4.58	9.6	5.05	1635 sh, 1625,	1100,		26	17 900, 13 300 sh, 10 000
	Found 36.92	3.68	4.25	9.8	(298)	1595, 1570 sh	1045			
Co(O-en-N-tm)I ₂ (brown)	Calcd 36.74	3.25	4.51	9.5	4.93	1640 sh, 1620,			12	21 700 sh, 18 500 sh, 10 200
	Found 36.48	3.32	4.81	9.9	(299)	1600, 1575 sh				
Co(O-en-N-tm)(NCS) ₂ (orange)	Calcd 52.17	4.17	11.59	12.2	4.78	1650 sh, 1630,	2075		4	20 800 sh, 10 500, 7000 sh
	Found 52.13	4.32	11.00	12.5	(299)	1595, 1575 sh				
Co(O-en-N-tm)(NCS) ₂ (purple)	Calcd 52.17	4.17	11.59	12.2	4.77	1640, 1635,	2085		4	20 000 sh, 11 000, 7700 sh
	Found 52.05	4.25	10.90	12.4	(298)	1600, 1575 sh	2060			
Co(Cl ₂ Ph ₂ -O-en-N-en)Cl ₂ (blue)	Calcd 55.84	3.75	4.34	9.1	4.50	1655, 1605,			1	17 000, 15 400, 9100, 7000
	Found 55.86	3.95	4.55	9.3	(297)	1585, 1570 sh				17 000 (585), 15 600 (325), 9500 (18), 7000 (46)
Co(Cl ₂ Ph ₂ -O-en-N-en)Br ₂ (green)	Calcd 49.07	3.30	3.82	8.0	4.64	1645, 1605,			1	15 400, 9300, 6700,
	Found 48.91	3.57	3.96	7.7	(298)	1585, 1565 sh				16 400 (515), 15 200 (505), 9100 (26), 6800 (62)
Co(Cl ₂ Ph ₂ -O-en-N-pn)I ₂ (brown)	Calcd 44.21	3.11	3.32	7.0	4.57	1660, 1650 sh,			10	15 400, 10 400, 7700, 6700 sh
	Found 44.55	3.10	3.14	7.2	(296)	1590, 1570 sh				

^a Color of complex in parentheses. ^b In Bohr magnetons; temperature of determination in parentheses (K). ^c Conductivity ($\Omega^{-1} \text{ cm}^{-2} \text{ mol}^{-1}$) in nitrobenzene at 23 °C. ^d Solid-state reflectance spectra; values in brackets are solution spectra (dichloromethane); ϵ values in parentheses. All spectra also contain a high-intensity charge-transfer band.

Table II. Refined Atomic Positional and Isotropic Thermal Parameters

Atom	x^a	y	z	$10^2 U_{iso},^b \text{ \AA}^2$
Co	0.0504 (2)	0.2048 (1)	0.2175 (1)	
S(1)	0.0686 (4)	0.4204 (2)	0.0469 (2)	
S(2)	0.3344 (5)	0.0654 (2)	0.0285 (3)	
O(1)	-0.0881 (8)	0.2688 (3)	0.3147 (5)	6.0 (2)
O(2)	0.2368 (8)	0.2291 (3)	0.3379 (5)	5.9 (2)
N(1)	0.058 (1)	0.3020 (5)	0.1576 (6)	7.1 (3)
N(2)	0.192 (1)	0.1557 (6)	0.1376 (7)	8.2 (3)
N(3)	-0.191 (1)	0.1779 (5)	0.1576 (6)	6.8 (3)
N(4)	0.051 (1)	0.1043 (5)	0.2889 (6)	6.5 (3)
C(1)	0.062 (1)	0.3527 (6)	0.1117 (7)	5.1 (3)
C(2)	0.253 (1)	0.1176 (6)	0.0924 (8)	6.9 (4)
C(3)	-0.223 (1)	0.3099 (6)	0.2786 (8)	6.1 (4)
C(4)	-0.253 (1)	0.3763 (6)	0.3160 (8)	7.3 (4)
C(5)	-0.398 (2)	0.4129 (8)	0.282 (1)	10.3 (5)
C(6)	-0.512 (2)	0.3841 (8)	0.2134 (9)	9.8 (5)
C(7)	-0.482 (2)	0.3196 (7)	0.1764 (9)	8.6 (4)
C(8)	-0.336 (1)	0.2802 (6)	0.2060 (8)	6.4 (4)
C(9)	-0.317 (1)	0.2131 (6)	0.1591 (8)	7.0 (4)
C(10)	-0.204 (2)	0.1100 (6)	0.1062 (9)	8.6 (4)
C(11)	-0.156 (2)	0.0465 (7)	0.169 (1)	10.8 (5)
C(12)	-0.098 (2)	0.0618 (7)	0.2718 (9)	9.8 (5)
C(13)	0.180 (1)	0.0757 (6)	0.3362 (8)	6.4 (4)
C(14)	0.334 (1)	0.1081 (6)	0.3668 (7)	5.9 (3)
C(15)	0.473 (1)	0.0636 (7)	0.4019 (8)	8.0 (4)
C(16)	0.621 (2)	0.0930 (7)	0.4343 (9)	8.8 (4)
C(17)	0.648 (2)	0.1648 (7)	0.4362 (9)	9.4 (4)
C(18)	0.517 (1)	0.2112 (7)	0.4005 (8)	7.3 (4)
C(19)	0.369 (1)	0.1796 (6)	0.3688 (7)	6.1 (3)
C(20)	0.160 (1)	0.2535 (7)	0.4135 (7)	8.3 (4)
C(21)	0.029 (2)	0.3031 (7)	0.3849 (9)	8.8 (4)

^a The standard deviation of the least significant digit is included in parentheses in this and subsequent tables. ^b Anisotropic thermal parameters are given in Table III.

Table III. Anisotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$)^a

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	7.7 (1)	5.7 (1)	4.35 (9)	-0.5 (1)	1.22 (8)	0.65 (9)
S(1)	12.1 (3)	5.0 (2)	6.6 (2)	0.0 (2)	1.7 (2)	6.6 (2)
S(2)	13.1 (4)	10.5 (3)	9.3 (3)	3.3 (3)	1.6 (3)	-2.4 (3)

^a The anisotropic temperature factor expression is of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + U_{23}klb^*c^*)]$.

Table IV. Interatomic Bond Lengths (\AA)

Co-O(1)	2.325 (7)	C(8)-C(9)	1.45 (1)
Co-O(2)	2.170 (7)	C(9)-N(3)	1.24 (1)
Co-N(1)	2.01 (1)	N(3)-C(10)	1.46 (1)
Co-N(2)	2.03 (1)	C(10)-C(11)	1.50 (2)
Co-N(3)	2.089 (9)	C(11)-C(12)	1.53 (2)
Co-N(4)	2.140 (9)	C(12)-N(4)	1.45 (1)
N(1)-C(1)	1.16 (1)	N(4)-C(13)	1.27 (1)
N(2)-C(2)	1.15 (1)	C(13)-C(14)	1.41 (1)
C(1)-S(1)	1.58 (1)	C(14)-C(15)	1.43 (1)
C(2)-S(2)	1.59 (1)	C(14)-C(19)	1.36 (1)
O(1)-C(3)	1.38 (1)	C(15)-C(16)	1.35 (2)
O(1)-C(21)	1.43 (1)	C(16)-C(17)	1.35 (2)
C(3)-C(4)	1.39 (1)	C(17)-C(18)	1.41 (2)
C(3)-C(8)	1.40 (1)	C(18)-C(19)	1.36 (1)
C(4)-C(5)	1.39 (1)	C(19)-O(2)	1.44 (1)
C(5)-C(6)	1.36 (2)	O(2)-C(20)	1.46 (1)
C(6)-C(7)	1.36 (2)	O(20)-C(21)	1.42 (1)
C(7)-C(8)	1.41 (1)		

perchlorate absorptions (ν_3) at 1100 cm^{-1} which are asymmetric in each case but it is not possible from this to decide whether ionic or bound perchlorates are present.¹¹ The magnetic moments (Table I) are typical of high-spin octahedral or five-coordinate cobalt(II) complexes since the values fall in the expected range of $4.7\text{--}5.2 \mu_B$.¹²

The solid-state reflectance spectra (Table I) are consistent with the complexes having five-coordinate structures.¹³ Al-

Table V. Selected Interatomic Angles (deg)

O(1)-Co-O(2)	75.5 (3)	C(7)-C(8)-C(3)	116 (1)
O(1)-Co-N(1)	82.7 (3)	C(7)-C(8)-C(9)	118 (1)
O(1)-Co-N(2)	174.0 (3)	C(3)-C(8)-C(9)	126 (1)
O(1)-Co-N(3)	80.7 (3)	C(8)-C(9)-N(3)	129 (1)
O(1)-Co-N(4)	95.5 (3)	C(9)-N(3)-C(10)	119 (1)
O(2)-Co-N(1)	95.7 (3)	Co-N(3)-C(9)	127.8 (9)
O(2)-Co-N(2)	99.6 (3)	Co-N(3)-C(10)	113.4 (7)
O(2)-Co-N(3)	150.9 (3)	N(3)-C(10)-C(11)	112 (1)
O(2)-Co-N(4)	81.0 (3)	C(10)-C(11)-C(12)	118 (1)
N(1)-Co-N(2)	94.4 (4)	C(11)-C(12)-N(4)	112 (1)
N(1)-Co-N(3)	97.7 (4)	C(12)-N(4)-C(13)	118 (1)
N(1)-Co-N(4)	176.5 (4)	Co-N(4)-C(12)	117.7 (8)
N(2)-Co-N(3)	105.1 (4)	Co-N(4)-C(13)	123.7 (8)
N(2)-Co-N(4)	87.0 (4)	N(4)-C(13)-C(14)	128 (1)
N(3)-Co-N(4)	85.0 (4)	C(13)-C(14)-C(15)	119 (1)
Co-N(1)-C(1)	170.4 (9)	C(13)-C(14)-C(19)	127 (1)
Co-N(2)-C(2)	167 (1)	C(15)-C(14)-C(19)	114 (1)
N(1)-C(1)-S(1)	179 (1)	C(14)-C(15)-C(16)	121 (1)
N(2)-C(2)-S(2)	179 (1)	C(15)-C(16)-C(17)	123 (1)
Co-O(1)-C(3)	120.4 (6)	C(16)-C(17)-C(18)	119 (1)
Co-O(1)-C(21)	108.9 (6)	C(17)-C(18)-C(19)	117 (1)
C(3)-O(1)-C(21)	115.4 (8)	C(18)-C(19)-C(14)	127 (1)
O(1)-C(3)-C(4)	122 (1)	C(18)-C(19)-O(2)	115 (1)
O(1)-C(3)-C(8)	117 (1)	C(14)-C(19)-O(2)	118 (1)
C(4)-C(3)-C(8)	121 (1)	C(19)-O(2)-C(20)	112.0 (8)
C(3)-C(4)-C(5)	120 (1)	Co-O(2)-C(19)	120.7 (6)
C(4)-C(5)-C(6)	121 (1)	Co-O(2)-C(20)	110.0 (6)
C(5)-C(6)-C(7)	119 (1)	O(2)-C(20)-C(21)	113 (1)
C(6)-C(7)-C(8)	123 (1)	C(20)-C(21)-O(1)	168 (1)

though the d-d spectra are partially obscured by strong charge-transfer absorptions which extend into the visible region, the five-coordinate geometry is suggested by the presence of a band near 14000 cm^{-1} ¹⁴ which in each spectrum occurs as a shoulder on the charge-transfer band.

The conductance values in nitrobenzene also suggest that these complexes are five-coordinate. The values are in the range $25\text{--}27 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and are thus typical of 1:1 electrolytes in this solvent.¹⁵ However for the hydrated complexes the possibility of six-coordination cannot be ruled out from the evidence above.

The complex $\text{Co}(O\text{-en-N-tn})_2$ appears to have a distorted octahedral structure. The reflectance spectrum is in accord with such a geometry¹⁶ and contains no band or shoulder near 14000 cm^{-1} (which, as mentioned above, indicates a five-coordinate geometry). Moreover this complex has a conductivity in nitrobenzene (Table I) which is considerably less than the value expected for a 1:1 electrolyte.

The above cobalt(II) complexes of *O-en-N-tn* are insufficiently soluble in commonly used solvents for solution spectra to be run.¹⁷ Previous work¹⁸ has demonstrated that phenyl substitution at the imine carbon atoms increases the solubility (in a range of nondonor solvents) of complexes of related noncyclic ligands. It has been shown also that because of steric interactions, each phenyl ring substituent will very likely be orientated approximately orthogonal to the plane of the adjacent backbone aromatic ring.¹⁹ Thus, in an attempt to obtain more soluble complexes (which would in turn give access to a wider range of physical measurements—both in the present study and for other studies planned for the future), the substituted macrocycles II and III were prepared from the diketone IV. Condensation with diamines occurred much less readily with the diketone IV than with the dialdehyde used previously,⁵ presumably due (in part) to the steric effects of the phenyl substituents. Reasonable yields of II and III were obtained by the direct condensation procedure in the absence of solvent outlined in the Experimental Section. Both compounds gave strong parent ion peaks in their respective mass spectra.

The cobalt(II) complexes of these substituted macrocyclic ligands are appreciably more soluble than the complexes of I in solvents such as dichloromethane, chloroform, benzene,

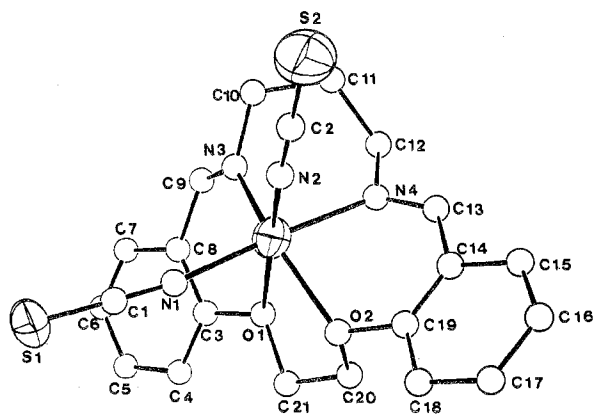


Figure 1. Molecular configuration of $\text{Co}(\text{O-en-N-tn})(\text{NCS})_2$, with the atom labels as used in Tables II-V.

or acetone. They are all high spin with magnetic moments in the 4.5–4.7- μ_B range (Table I). The solution and solid-state reflectance spectra are similar to each other and are compatible with low-symmetry octahedral complexes;¹⁶ strong additional evidence for six-coordinate structures is that all complexes have conductivities approaching those of nonelectrolytes in nitrobenzene (Table I).

During the synthesis of $\text{Co}(\text{O-en-N-tn})(\text{NCS})_2$, two different crystalline precipitates were isolated—an orange product and a purple product. Both were shown by elemental analyses, conductivity measurements, and infrared spectra to be of the type $\text{Co}(\text{O-en-N-tn})(\text{NCS})_2$. The two solids show different infrared thiocyanate stretching frequencies, namely, 2075 cm^{-1} for the orange product and a split absorption (2085, 2060 cm^{-1}) for the purple compound. The positions of the thiocyanate bands in each complex suggest that the thiocyanates are coordinated through their nitrogen atoms in each case.¹⁹ An attempt to study the interconversion of the two isomers in solution was inconclusive.¹⁷

The visible reflectance spectra for the two isomers of $\text{Co}(\text{O-en-N-tn})(\text{NCS})_2$ (Table I) are of little value for deciding structural differences between these products and hence an x-ray structure determination on the purple isomer has been performed.

The x-ray structure confirms a six-coordinate geometry for this complex with bonds from the cobalt to the nitrogen atoms of the thiocyanate anions and to the imine nitrogen and ether oxygen atoms of the macrocycle (see Figure 1).²⁰ The macrocyclic ligand does not present a planar N_2O_2 donor set to the cobalt atom but is folded giving a β -cis configuration (see Figure 2). Each of the three pairs of similar donors is arranged in a cis manner in the complex. The complexes are well separated in the solid state with closest intermolecular contacts being 2.38 Å between methylene hydrogen atoms of C(10) and C(21) and 2.68 Å between the C(2) atom and a methylene hydrogen atom of C(20).

The coordination polyhedron associated with the cobalt atom is markedly distorted from an octahedron (see Tables V and VI). It is probable that the folding of the macrocycle described above contributes significantly to the angular distortions because in this configuration the chelate ring sizes are not sufficient to allow the adjacent donors to span cis-coordination sites with retention of favorable metal-donor distances. Thus the four angles defined at the cobalt by adjacent donors in the macrocycle are all less than 85° (mean 80.6°) and the two trans donors in the macrocycle give $\text{O}(2)\text{-Co-N}(3) = 150.9(3)^\circ$.

In addition to these angular distortions the lengths of bonds from the cobalt atom show significant variations. The $\text{Co-O}(1)$ bond which is trans to a thiocyanate ligand is longer (2.325 (7) Å) than the $\text{Co-O}(2)$ bond (2.170 (7) Å). Similarly

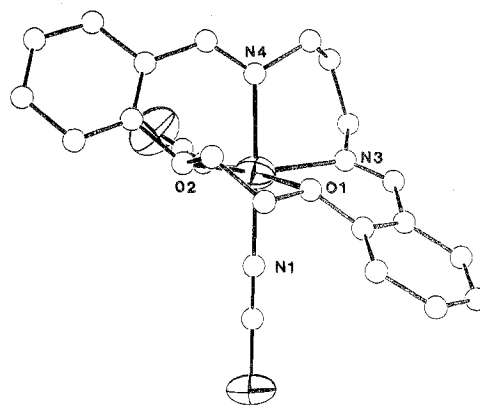
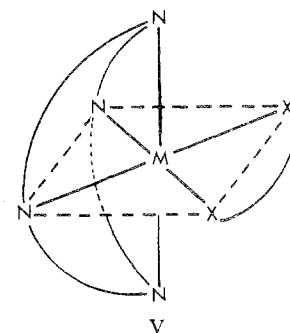


Figure 2. Molecular configuration of $\text{Co}(\text{O-en-N-tn})(\text{NCS})_2$, showing the folding of the macrocycle about the line $\text{O}(2)\text{-N}(3)$.

the $\text{Co-N}(4)$ bond distance (2.140 (9) Å) is greater than for $\text{Co-N}(3)$ (2.089 (9) Å).

The cobalt bonds to the weak ether donors are significantly longer than the sum of the covalent radii, 1.98 Å (octahedral $\text{Co}(\text{II})$, 1.32 Å; O, 0.66 Å)²¹ and also longer than the Co-O distances with anionic salicylaldimine ligands.²² On the basis of the ligand "bite" distances $\text{O}(1)\text{-O}(2) = 2.75$ Å, $\text{O}(1)\text{-N}(3) = 2.86$ Å, $\text{O}(2)\text{-N}(4) = 2.80$ Å, and $\text{N}(3)\text{-N}(4) = 2.86$ Å, the "hole" which would be defined by a planar form of the ligand would provide metal-donor distances in the range 1.96–2.02 Å, values which are similar to those observed in comparable macrocycles with planar " N_4 " donor sets.²³ Consequently a factor which may favor the folding of the macrocycle about the $\text{O}(2)\text{-N}(3)$ axis is that the resulting cis configuration allows the formation of longer bonds from the ether oxygen atoms to the cobalt.

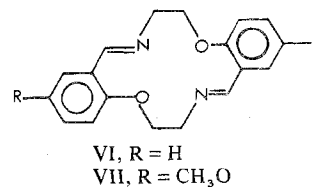
Other previously reported examples of folded configurations for quadridentate macrocyclic ligands in six-coordinate complexes mainly involve " N_4 " ligands (e.g., the Curtis type).²⁴ In such cases, the macrocycles are forced to adopt a cis configuration of type V about the metal ion by the presence



of a coordinating bidentate ligand which occupies cis positions in the octahedral coordination sphere.

In a few cases²⁵ noncyclic quadridentate salicylaldimine ligands of the "salen" type have been found to adopt cis-octahedral configurations. Such configurations are a necessary consequence of the fact that in these complexes the remaining two octahedral sites are spanned by a bidentate ligand.

The trans-imine ligands VI and VII are closely related to



O-en-N-tn and have been shown to give nickel(II) iodide

complexes with *trans*²⁶ and *cis*²⁷ configurations, respectively. In the *cis* complex Ni(VII)I₂ the nickel–oxygen distances, 2.25 and 2.18 Å, and the nickel–nitrogen distances, 2.06 and 2.03 Å, are significantly longer than in the *trans* complex and compare more closely with the analogous cobalt bonds in Co(*O-en-N*-tn)(NCS)₂.

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Registry No. II, 62375-57-9; III, 62375-56-8; IV, 25440-16-8; [Co(*O-en-N*-tn)Cl]ClO₄, 62393-00-4; [Co(*O-en-N*-tn)Br]ClO₄, 62392-98-7; [Co(*O-en-N*-tn)I]ClO₄, 62431-04-3; Co(*O-en-N*-tn)I₂, 62392-96-5; *trans*-Co(*O-en-N*-tn)(NCS)₂, 62445-35-6; *cis*-Co(*O-en-N*-tn)(NCS)₂, 62392-95-4; Co(Cl₂Ph₂-*O-en-N-en*)Cl₂, 62392-94-3; Co(Cl₂Ph₂-*O-en-N-en*)Br₂, 62392-93-2; Co(Cl₂Ph₂-*O-en-N-pn*)I₂, 62448-24-2.

Supplementary Material Available: Listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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Synthesis, Properties, and X-Ray Structural Characterization of Cationic Five-Coordinate σ -Alkylnickel(II) Compounds with Poly(tertiary phosphines and arsines)

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Cationic five-coordinate nickel(II) compounds containing a nickel–carbon σ bond with the general formula [NiR(L)]BPh₄ (L = tris(2-diphenylphosphinoethyl)amine, np₃; tris(2-diphenylarsinoethyl)amine, nas₃; tris(2-diphenylphosphinoethyl)phosphine, pp₃; R = CH₃, C₂H₅, or CH₂C₆H₅) were synthesized by reaction of the five-coordinate complexes [NiX(L)]BPh₄ (X = halogen) with the appropriate Grignard reagents. The structure of the [Ni(CH₃)(np₃)]BPh₄·CH₃COCH₃ derivative was determined by x-ray analysis using diffractometric data. The crystals are monoclinic, space group *P*2₁/*c* with cell dimensions *a* = 12.514 (2) Å, *b* = 20.234 (3) Å, *c* = 24.214 (4) Å, β = 103.23 (2)°. The structure was solved by three-dimensional Patterson and Fourier syntheses and refined by least-squares techniques to a final conventional *R* factor of 0.061 over the 1738 independent observed reflections. The structure consists of [Ni(CH₃)(np₃)]⁺ cations, of tetraphenylborate anions, and of interposed acetone molecules. The chromophore is a distorted trigonal bipyramid with the methyl group linked to the nickel in an axial position, the Ni–C distance being 2.02 (2) Å. An analogous trigonal-bipyramidal geometry is assigned to all of the σ -carbon-bonded complexes on the basis of physical data.

Introduction

Most of the alkyl- and arylnickel(II) complexes so far described are four-¹ or six-coordinate.² Apart from the cyclopentadienyl derivatives,³ which only formally can be

considered as five-coordinate, only two five-coordinate organonickel complexes have been reported, namely, [((CH₃)₃P)₄Ni(CH₃)]⁺,² and [Ni(C₆H₅)(nas₃)]⁺,⁴ where nas₃ is the tripod tetradentate ligand tris(2-diphenylarsino-