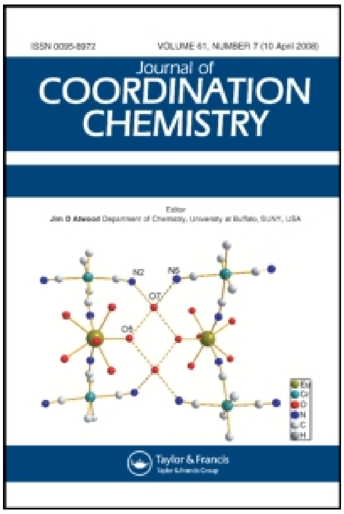

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MIXED-LIGAND COMPLEXES OF COBALT(III) WITH DITHIOCARBAMATES AND A CYCLIC TETRADENTATE SECONDARY AMINE

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MIXED-LIGAND COMPLEXES OF COBALT(III) WITH DITHIOCARBAMATES AND A CYCLIC TETRADENTATE SECONDARY AMINE

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4-Morpholine-, piperidine-, 4-piperazine- and *N*-methyl- piperazine-dithiocarbamate complexes of Cobalt (III) with 1, 4, 8, 11-tetraazacyclotetradecane, of general formula [Co(Rdtc)cyclam] $(C10_4)_2$, have been prepared and have been characterized. The complexes adopt *cis*-octahedral geometry with folded macrocyclic ligand and with the dithiocarbamate bound as a bidentate. *trans*-influence of the dithiocarbamate ligands was studied by NMR spectroscopy and established the order piperidine-dtc >4-morpholine-dtc>*N*-methyl-piperazine-dtc.

Keywords: cobalt(III); macrocycles; dithiocarbamates; synthesis; complexes

INTRODUCTION

Transition metal, mixed ligand complexes are essential for a study of mutual ligand influences. In the case of dithiocarbamate ligands the investigation is hampered by the high tendency to MS_6 coordination. Although many complexes of heterocyclic dithiocarbamate ligands have been investigated,[1–7] only a few mixed ligand complexes have been reported.[8–9] To achieve a stable mixed ligand dithiocarbamate complexes one must combine dithiocarbamates with other ligands of comparable ligating ability. In that respect macrocyclic ligands are especially suitable. We have been investigating cobalt(III) complexes of 1, 4, 8, 11-tetraazacyclotetradecane (cyclam), a macrocyclic ligand which forms mixed ligand complexes with diverse monodentate[10–14] and bidentate ligands.[15–17] Cyclam is suitable for the preparation of *cis*-CoN_4S_2 complexes of dithiocarbamates.

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In the present paper we report the synthesis, molecular structure and spectroscopic properties of cobalt(III) cyclam dithiocarbamate complexes. Four dithiocarbamate ligands, 4-Morpholine- (morphdtc), piperidine- (pipdtc), 4-piperazine-(pzdtc) and *N*-methyl- piperazine- (CH_3-pzdtc) - dithiocarbamates were investigated for their *trans*-influence.

EXPERIMENTAL

Synthesis

The sodium salts of Rdtc were obtained according to the procedure described in the literature.[7] High purity grade commercial cyclam from Aldrich Chemical Co. was used without further purification.

A mixture of 1 mmol (360 mg) of cobalt(II) perchlorate hexahydrate and 1 mmol (200mg) of cyclam dissolved in a minimum amount of ethanol-water mixture (5:1, v/v) was stirred and air bubbled through the solution for 30 minutes. Then, dithiocarbamate solution (1mmol) was added slowly with continuous stirring, air-bubbling and heating on a water bath at 60°C for 3 hours. The mixture was allowed to cool to room temperature and crystalline products of the corresponding complexes were filtered off; (**I**), *cis*-[Co(morphdtc)cyclam] $(C1O_4)_4$, reddish-brown. Yield: 81 mg (13%). *Anal.* Calcd. for $CoC_{15}H_{32}N_5S_2O_9Cl_2$(%): C, 29.04; H, 5.20; N, 11.29. Found: C, 28.92; H, 5.47; N, 11.34; (**II**), *cis*-[Co(pipdtc)cyclam] $(C1O_4)_2$, purple. Yield: 88 mg (14%). *Anal.* Calcd. for $CoC_{16}H_{34}N_5S_2O_8Cl_2$(%): C, 31.08; H, 5.54; N, 11.32. Found: C, 31.13; H, 5.64; N, 11.21; (**III**), *cis*-[Co(pzdtc)cyclam] $(C1O_4)_2$, pink. Yield: 57 mg (9%). *Anal.* Calcd. for $CoC_{15}H_{33}N_6S_2O_8Cl_2$(%): C, 29.08; H, 5.37; N, 13.56. Found: C, 28.98; H, 5.41; N, 13.08; (**IV**) *cis*-[Co(CH_3-pzdtc)cyclam] $(C1O_4)_2$, violet. Yield: 52 mg (8%). *Anal.* Calcd. for $CoC_{16}H_{35}N_6S_2O_8Cl_2$(%): C, 30.34; H, 5.57; N, 13.26. Found: C, 30.54; H, 5.80; N, 13.28.

Electronic and IR spectra

Electronic spectra were recorded on a GBC UV/VIS 911A spectrophotometer. Infrared spectra in the 4000-400 cm^{-1} range were measured on a Perkin Elmer 317 25× FTIR spectrophotometer, using the KBr disk technique. Far IR spectra were measured on a Perkin Elmer 983 instrument using Nujol mull supported between CsI sheets.

NMR measurements

Complexes **I, II** and **IV** were dissolved (0.05 M) in DMSO-d_6. **III** was too insoluble for measurement. All NMR spectra were recorded on a Bruker AMX-300 spectrometer at room temperature. Proton and carbon chemical shifts were determined relative to TSP, and nitrogen chemical shifts were referenced to nitromethane *via* the proton resonance of internal TSP using the resonance ratio $\omega(^{15}N)/\omega(^{1}H) = 0.10136783$. ^{59}Co chemical shifts were referenced to an external standard of aqueous $K_3[Co(CN)_6]$.

1D ^{13}C spectra were recorded with 20000 scans and a repetition rate of 2s and 1D ^{59}Co spectra were recorded with 10000 scans and a 0.5s repetition rate. 2D ^1H—^{13}C and ^1H—^{15}N chemical shift correlation spectra were obtained by heteronuclear multiple quantum coherence transfer (HMQC) over one bond coupling ($^1J_{HC} \sim 130$ Hz or $^1J_{HN} \sim 95$ Hz) applying the 2D pulse sequence described in ref. 18. For 2D ^1H—^{13}C spectra, 300 increments in the evolution domain were collected, each recorded with 64 scans and a repetition rate of 1 s. For 2D ^1H—^{15}N spectra, 200 increments were collected, each recorded with 512 scans and a repetition rate of 0.6 s. Two-dimensional proton-proton chemical shift correlated spectra were recorded by 2D DFCOSY (*d*ouble quantum *f*ilter *co*rrelated *s*pectroscop*y*),[19] with 512 increments, 16 scans and a repetition rate of 1.5 s.

RESULTS AND DISCUSSION

SYNTHESIS

Cis-[Co(Rdtc)cyclam] $(ClO_4)_2$ complexes were obtained by direct synthesis and isolated by crystallization from the reaction mixture in a yield of about 10%. This simple method of preparation is based on the high stability of the Co(cyclam) chelate. The compounds are microcrystalline, soluble in water, dimethylsulfoxide and *N,N'*-dimethylformamide, and insoluble in chloroform, dichlormethane and acetone. The pzdtc complex is sparingly soluble in all the above solvents.

Electronic absorption spectra

The complexes have very similar absorption spectra in the 518–530 nm range with one well-resolved band. The absorbance at 530 ($\epsilon = 277$); 525 ($\epsilon = 257$); 518 ($\epsilon = 153$); 527 nm ($\epsilon = 198\ M^{-1}\ cm^{-1}$) for **I** to **IV**, respectively, can be related to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition.[20] The $^1A_{1g} \rightarrow {}^1T_{2g}$ transition is obscured by charge transfer bands, especially due to the NCS_2 chromophore.[21–23] However, it appears as shoulder for **I** and **II** at 433 (ϵ = 227) and 434 nm (ϵ = 231).

IR Spectra

Relevant cobalt(III) cyclam bands of *cis*-[Co(Rdtc)cyclam]$(C10_4)_2$ complexes are listed in Table I. The 800–910 cm^{-1} region is of considerable interest because it differs for *cis* and *trans* isomers of well-characterized cobalt(III) cyclam complexes.[24, 17] It is claimed that in this region no *trans* isomers have more than three bands, while the less symmetrical *cis*-isomers have at least five bands. The appearance of five bands in the spectra of the newly synthesized complexes clearly indicates a *cis* configuration. The ν(N—H) vibrations located in the 3100–3200 cm^{-1} region suggest coordination of cyclam, whereas bands of ionic perchlorate[23] are located at about 1110 cm^{-1} (ν(ClO_4) vs) and 625 cm^{-1} (δ($C10_4$)w).

The most informative bands for Rdtc coordination (ν(C—N), n(C—S) and ν(Co—S)) are given in Table II. The nature of the heterocyclic ring in the complexes has very small effect on these bands. Bands assigned to ν(C—N), in the 1460–1490 cm^{-1} range, reflect the partial double bond character of C—N because ν(C—N) and ν(C═N) are expected in the ranges 1350–1250 cm^{-1} and 1690–1640 cm^{-1}, respectively.[1] The number of bands for ν(C—S) in the 950–1050 cm^{-1} region could serve as a diagnostic of mono- or bidentate coordination[25] of Rdtc ligands. The presence of only one strong band in the region at about 1000 cm^{-1} indicates bidentate coordination. Finally, bands corresponding to ν(Co—S) located in the far IR (300–350 cm^{-1}) are in good agreement with available literature data.[2]

TABLE I Absorption bands (cm^{-1}) in the 800–910 and 3100–3200 cm^{-1} regions for the complexes

	ρ(N—H)	*ρ(CH_2)*	*ν(N—H)*
I	877s*; 860w; 855m;	819sh; 806vs;	3230m 3139m
II	890s; 876w; 860m;	818sh; 805vs;	3224m 3119m
III	891s; 888w; 869m;	822sh; 807vs;	3219m 3117m
IV	905s; 891w; 880m;.	822sh; 812vs;	3219m 3127m

* Abbreviations: s, strong; w, weak; m, medium; sh, shoulder; vs, very strong.

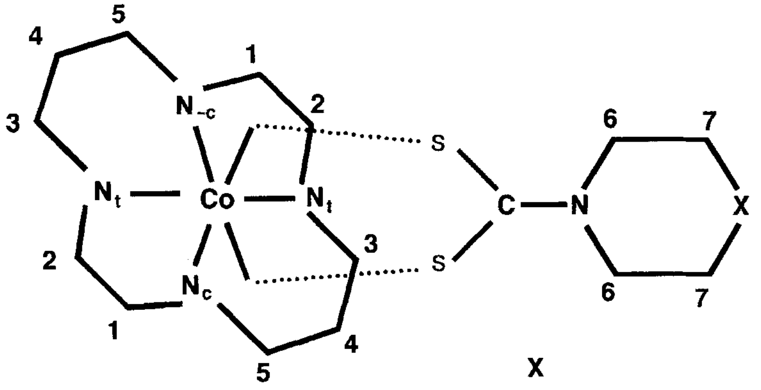
TABLE II Absorption bands (cm^{-1}) of the free and coordinated Rdtc ligands

	ν(C—N)	ν(C—S)	ν(Co—S)
MorphdtcNa	1449s*	991s	
PipdtcNa	1451s	969s	
PzdtcNa	1463s	970s	
CH_3—PzdtcNa	1449s	997s	
I	1466s	1012s	338w
II	1465s	1008s	339w
III	1488s	983s	340w
IV	1462s	1039s	340w

* Abbreviations: s, strong; w, weak.

NMR spectra

The heteronuclear ^1H—^{13}C and ^1H—^{15}N and homonuclear ^1H—^1H chemical shift correlation spectra enabled assignment of all resonances in the ^1H, ^{13}C, ^{15}N spectra. High symmetry of the complexes was reflected in the chemical shift degeneracy of all the chemically equivalent nuclei in the ligands (Table III and Scheme 1). Intensities are consistent with the assumed composition of the complexes (1:1 ratio of cyclam *vs* dtc resonances). All chemical shifts are in the expected regions, but show subtle differences in going from complex to complex. ^{59}Co chemical shifts (Table III) give direct information on the complex chromophore and they are at position which correspond to a CoN_4S_2 ligand field.[26] The spectroscopic data are consistent with *cis*-octahedral geometry for the complexes, which implies a folded conformation of the macrocyclic ligand and dithiocarbamates bonded as bidentates (Scheme 1).



I, O(morphdtc); II, CH_2 (pipdtc); III, N (CH_3pzdtc); IV, N-CH_3 (CH_3pzdtc).

Scheme 1

TABLE III ^{1}H, ^{13}C, ^{15}N and ^{59}Co NMR data for the complexes

					$^{1}H^{a}$					
	$H(N_c)$	$H(N_t)$	$H_2(C1)$	$H_2(C2)$	$H_2(C3)$	$H_2(C4)$	$H_2(C5)$	$H_2(C6)$	$H_2(C7)$	$H(x)$
I	7.52	5.90	2.90; 2.07	2.83; 2.25	2.68; 2.00	1.89; 1.67	2.68; 1.88	3.98	3.76	
II	8.28	5.78	2.81; 2.03	2.90; 2.21	2.70; 1.98	1.90; 1.62	2.60; 1.88	3.92	1.71	1.7-1.6
IV	6.57	5.88	3.00; 2.21	2.69; 2.28	2.70; 2.00	1.1-1.8	2.80; 1.92	3.95	2.52	2.70
						$^{13}C^{a}$				
	S_2CN	$C1$	$C2$	$C3$	$C4$	$C5$	$C6$	$C7$	Cx	
I	198.84	53.76	48.69	46.74	21.18	48.80	47.83	65.24		
II	197.10	53.76	48.80	46.60	20.98	48.91	48.46	24.45	25.11	
IV	198.02	53.62	48.59	46.58	21.28	48.59	47.30	53.23	45.06	
		$^{15}N^{b}$	$^{59}Co^{c}$							
	N_c	N_t								
I	−382.7	−384.1	7461	(1.4)						
II	−385.0	−383.8	7444	(2.5)						
IV	−381.3	−385.0	7457	(2.3)						

[a] In ppm relative to TMP. [b] In ppm relative to neat nitromethane. [c] In ppm relative to $K_3[Co(CN)_6]$; line width in kHz. Notations of the resonances are according to Scheme 1.

The mutual ligand influence is evidenced in the NMR spectra. Difference in the *trans*-influence of the dtc-ligands on the amide proton and nitrogen chemical shifts of cyclam is quite pronounced (Table 3). The deshielding effect on these resonances is an indication of the stronger metal-ligand bond of the corresponding dithiocarbamate ligand[27] and the *trans*-influence ordering of the ligand is **pipdtc** > **morphdtc** > **CH_3pzdtc**. Further evidence for such ordering is seen in the ^{13}C chemical shift of the $-CS_2$ group. Dithiocarbamate ligands of greater *trans*-influence have a more shielded $-CS_2$ carbon, indicating greater electronic density of the ligating group.

Acknowledgments

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