

## PRELIMINARY STRUCTURE OF CIS-PIPERIDINE DITHIOCARBAMATO (1,4,8,11-TETRA-AZACYCLOTETRADECANE) COBALT(III) PERCHLORATE

*A new complex of cobalt(III) with 1,4,8,11-tetra-azacyclotetradecane (cyclam) and the heterocyclic dithiocarbamato ion as a bidentate ligand was prepared and characterized by X-ray analysis. The structure was identified as cis-piperidine dithiocarbamato(1,4,8,11-tetra-azacyclotetradecane)cobalt(III) perchlorate, [Co(pipdtc)cyclam] (ClO<sub>4</sub>)<sub>2</sub> and it can be described in terms of a cis-octahedral geometry with a folded cyclam configuration around the cobalt atom with the piperidine dithiocarbamato ion occupying the remaining two sites.*

Investigation of complexes with macrocyclic molecules with greater rigidity due to the presence of amine quadridentate ligands is of great theoretical and practical interest. The macrocyclic [14]aneN<sub>4</sub> *cyclam* (1,4,8,11-tetra-azacyclotetradecane) ligand exhibits an overriding tendency to coordinate to metal ions in a planar arrangement, favoring *trans* geometry with monodentate ligands [1], but in the corresponding *cis* complexes [2–5] it is forced into the folded form which can be favored especially with bidentate extracyclic ligands.

On the other hand, the dithiocarbamato group (*Rdtc*<sup>-</sup>) of ligands has been found to act as uninegative bidentate ligands, coordinating through both the sulphur atoms with many metal ions [6,7]. Transition metal complexes with these ligands have been extensively investigated and are of interest in many fields: as flotation agents, insecticides, in the number industry and as antifungal agents [8]; in medicine in the treatments of alcoholism and rheumatism [9]. Besides, these coordination compounds containing sulphur and nitrogen atoms are good corrosion inhibitors in acidic media [10,11].

Despite the considerable interest in metal dithiocarbamate complexes, relatively little has so far been done on the preparation and characterization of mixed-ligand complexes, especially with suitable macrocyclic ligand. In our previous papers [3,5] we reported the preparation and spectral assignments of a series of complexes with the general formula [Co(*Rdtc*)*cyclam*]<sup>2+</sup> (*Rdtc*<sup>-</sup> is a heterocyclic dithiocarbamato ligand, i.e., 4-morpholine, 4-thiomorpholine, 4-piperazine, N-methylpiperazine, piperidine, 2-, 3- or 4-methylpiperidine dithiocarbamate ion) in which the

*Rdtc*<sup>-</sup> anion acts as a S,S\*-bidentate ligand and the macrocycle *cyclam* adopts a folded conformation.

In the present paper, single-crystal X-ray analysis of the complex [Co(pipdtc)cyclam] (ClO<sub>4</sub>)<sub>2</sub>, is reported. This complex represents the first case where the heterocyclic *pipdtc* bidentate ligand in a mixed-ligand complex is presented.

### MATERIALS AND METHODS

#### General procedures

The sodium salts of *pipdtc* was obtained according to a procedure described in the literature [17]. Commercial high-purity grade *cyclam* from Aldrich Chemical Co. was used without further purification.

Elemental analyses (C, H, N) were performed by standard micromethods at the Department of Instrumental Analysis of the Faculty of Chemistry, Belgrade. Electronic spectra of the aqueous complexes solutions (1 · 10<sup>-3</sup> M) were recorded on a GBC UV/VIS 911 A spectrophotometer. IR spectra were measured in the 4000–400 cm<sup>-1</sup> range on a Perkin Elmer 317 25xFTIR spectrophotometer, using KBr discs. Far-IR spectra were measured on a Perkin Elmer 983G instrument using Nujol mull supported between CsI sheets. NMR spectra were recorded on a Bruker AMX-300 spectrometer at room temperature in DMSO-d<sub>6</sub>. <sup>1</sup>H and <sup>13</sup>C chemical shifts were determined relative to TSP, and <sup>15</sup>N chemical shifts were referenced to nitromethane *via* the proton resonance of the internal TSP using the resonance ratio ω(<sup>15</sup>N)/ω(<sup>1</sup>H) = 0.10136783. <sup>59</sup>Co chemical shifts were referenced to an external standard of aqueous K<sub>3</sub>[Co(CN)<sub>6</sub>]. All available data are described in the literature [3].

#### Synthesis and spectroscopic data of the cis-[Co(pipdtc)cyclam](ClO<sub>4</sub>)<sub>2</sub>

**Synthesis:** A mixture of 1mmol (360mg) of cobalt(II) perchlorate hexahydrate and 1mmol (200mg)

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Paper received: June 28, 2000  
Paper accepted: December 11, 2000

of *cyclam* dissolved in ethanol–water mixture (5:1, v/v) was stirred and bubbled with air for 30 minutes. A *Napipdtc* solution (1mmol) was added slowly with continuous stirring, air–bubbling and heating (60°) for 3 hours. After allowing the mixture to cool to room temperature, the crystalline product was separated and dried over CaCl<sub>2</sub>. A suitable single crystal for X–ray analysis was obtained by slow evaporation from the source solution. Yield 88 mg (14%). **Anal. Calcd.** for CoC<sub>16</sub>H<sub>34</sub>N<sub>5</sub>S<sub>2</sub>O<sub>8</sub>Cl<sub>2</sub> (%): C, 31.08; H, 5.54; N, 11.32. **Found:** C, 31.13; H, 5.64; N, 11.21. **UV/VIS** (H<sub>2</sub>O; λ, nm; ε, M<sup>-1</sup>cm<sup>-1</sup>): 525 (257), 434 (231). **IR** (KBr, cm<sup>-1</sup>): 3224m, 3119m, 1465s, 1110vs, 1008s, 890s, 876w, 860m, 818sh, 805vs, 625w. (Csl, cm<sup>-1</sup>): 339w. **<sup>1</sup>H NMR** (DMSO–d<sub>6</sub>, 300MHz, δ(ppm)): 8.28 (H, N1), 5.78 (H, N2), 2.81; 2.03 (2H, C1), 2.90; 2.21 (2H, C2), 2.70; 1.98 (2H, C3), 1.90; 1.62 (2H, C4), 2.60; 1.88 (2H, C5), 3.92 (2H, C7), 1.71 (2H, C8), 1.7–1.6 (2H, C9). **<sup>13</sup>C NMR** (DMSO–d<sub>6</sub>, 300MHz, δ(ppm)): 197.10 (S<sub>2</sub>CN), 53.76 (C1), 48.80 (C2), 46.60 (C3), 20.98 (C4), 48.91 (C5), 48.46 (C7), 24.45 (C8), 25.11 (C9). **<sup>15</sup>N NMR** (DMSO–d<sub>6</sub>, 300MHz, δ(ppm)): –385.0 (N1), –383.8 (N2). **<sup>59</sup>Co NMR** (DMSO–d<sub>6</sub>, 300MHz, δ(ppm)): 7444 (Co).

### X–ray crystal structure analysis

Single crystals suitable for X–ray structure determination were grown by slow evaporation of the reaction mixture solution to which ether had been added. Diffraction data were obtained on a Rigaku AFC7R automated diffractometer with graphite monochromated MoKα radiation and a rotating anode generator at a temperature of 20 ± 1°C.

The Unit cell parameters were determined using the setting angles of 25 carefully centered reflections in the range 31.76 < 2θ < 36.07° corresponded to a C–centered monoclinic cell. The weak reflections (I < 10.0σ(I)) were rescanned and the counts were accumulated to ensure good counting statistics. Pertinent crystallographic parameters are given in Table 1. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects. The structure was solved by the direct method and expanded using Fourier techniques. Refinement was carried out by full–matrix least–squares methods based on 1566 observed reflections (I > 3.00σ(I)). The cobalt atom was refined anisotropically, while the rest were refined isotropically. Plots of Σω(|F<sub>o</sub>| – |F<sub>c</sub>|)<sup>2</sup> versus |F<sub>o</sub>|, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. Calculations were carried out on an FACOM–M 780 computer using the UNICS III [13,14] program system. The positional parameters of non–hydrogen atoms are given in Table 2. Atomic scattering factors were taken from the literature [15].

Table 1. Crystal data and data collection details for the cis–[Co(pipdtc)cyclam](ClO<sub>4</sub>)<sub>2</sub> complex

Formula	CoC <sub>16</sub> H <sub>34</sub> N <sub>5</sub> S <sub>2</sub> O <sub>8</sub> Cl <sub>2</sub>
Mr	618.43
Crystal system	monoclinic
Space group	C2/c (#15)
a/Å	14.342(2)
b/Å	16.596(2)
c/Å	12.151(2)
β/°	106.430(10)
V/Å <sup>3</sup>	2774.2(5)
Z	8
D <sub>x</sub> /g cm <sup>-3</sup>	1.366
Crystal size	0.30x0.30x0.40
μ(MoKα)/cm <sup>-1</sup>	9.10
Scan mode	ω–2θ
2θ <sub>max</sub> (°)	50.0
Data collected	2646 total 2538 unique
R <sup>b</sup>	0.181
R <sub>w</sub> <sup>b</sup>	0.129
R1	0.176
F <sub>000</sub>	1128.00

<sup>a</sup>Common data: scan speed 16.0 °/min;

weighting scheme 1/σ<sup>2</sup>(F<sub>o</sub>) = [σ<sup>2</sup><sub>c</sub>(F<sub>o</sub>) + p<sup>2</sup>/4 F<sub>o</sub><sup>2</sup>]<sup>-1</sup>

<sup>b</sup>R = Σ||F<sub>o</sub>| – |F<sub>c</sub>|| / Σ|F<sub>o</sub>|

Table 2. Fractional positional parameters and thermal parameters of non–hydrogen atoms for cis–[Co(pipdtc)cyclam](ClO<sub>4</sub>)<sub>2</sub><sup>a</sup>

Atom	X / a	y / b	Z / c	Beq / Å <sup>2b</sup>
Co	0.5000(0)	0.2182(2)	0.7500(0)	5.82(8)
N1	0.593(1)	0.219(1)	0.673(1)	11.3(5)
N2	0.429(1)	0.136(1)	0.640(2)	12.1(5)
S1	0.4324(4)	0.3250(3)	0.6446(4)	8.70(1)
N3	0.500(0)	–0.019(1)	0.7500(0)	14.6(7)
Cl	0.2628(5)	–0.0969(4)	0.6512(6)	4.50(1)
O1	0.2900(1)	–0.0613(10)	0.5760(1)	15.3(5)
O2	0.301(2)	–0.074(1)	0.732(2)	19.4(7)
O3	0.249(2)	–0.155(2)	0.624(2)	12.3(8)
O4	0.175(2)	–0.083(1)	0.637(2)	21.9(8)
C1	0.712(6)	0.216(5)	0.833(7)	48(4)
C2	0.672(3)	0.149(2)	0.726(3)	20(1)
C3	0.565(2)	0.217(2)	0.530(2)	15.9(9)
C4	0.506(2)	0.133(1)	0.528(2)	14.2(7)
C5	0.386(2)	0.143(2)	0.518(2)	16.0(9)
C6	0.312(2)	0.143(1)	0.648(2)	12.1(6)
C7	0.556(2)	0.500(1)	0.849(2)	12.5(7)
C8	0.572(2)	0.582(2)	0.843(3)	16.1(9)
C9	0.688(2)	0.636(9)	0.852(2)	12.1(6)

<sup>a</sup>Values in parentheses are estimated standard deviations.

<sup>b</sup>The equivalent isotropic thermal parameter is taken as  $B_{eq} = 8/3 \pi^2 (\sum_i \beta_{ij} a_i a_j)$ .

## RESULTS AND DISCUSSION

All spectroscopic data for the *cis*-[Co(pipdtc)cyclam](ClO<sub>4</sub>)<sub>2</sub> complex clearly show that the early-suggested structure [3, 5] is formed and is typical for this series of complexes with *cyclam* macrocycle and additional chelate *Rdte*<sup>-</sup> ligand. The UV/VIS spectrum is in agreement with the spectra of analogous complexes described earlier [2-5] and the absorbencies can be related to the <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub> and <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>2g</sub> transitions of the central cobalt(III) ion. The characteristic IR bands in the 800-910 cm<sup>-1</sup> region are of considerable interest because they are different for *cis* (five bands) and *trans* isomers (three bands) of well-characterized cobalt(III) *cyclam* complexes [2-5,16]. The two strong bands in the 3230-3050 cm<sup>-1</sup> range that can be ascribed to the ν(N-H) vibration of the *cyclam* moiety suggest its folded conformation. The <sup>1</sup>H NMR spectra support this conclusion as well. The amine proton region could serve as a diagnostic feature of *cis* or *trans* configuration because in *cis* complexes two pairs of non-equivalent protons exist. However, the *cis* conformation of *cyclam* is predicted on the basis of minimum-strain arguments [2] for *cyclam* taking into account the anisotropy of cobalt(III) [17]. The high symmetry of the complex is reflected in the <sup>13</sup>C NMR spectrum as well. The dithiocarbamato ligand *pipdte* has a more shielded -CS<sub>2</sub> carbon, indicating a greater electronic density of the ligating group and a stronger metal-ligand bond. The <sup>59</sup>Co chemical shifts give direct information on the complex chromophore which corresponds to a CoN<sub>4</sub>S<sub>2</sub> ligand field [18]. All of these spectroscopic data are consistent with *cis*-octahedral geometry for the complex, which implies a folded conformation of the macrocyclic ligand and dithiocarbamato ligand bounded as S,S\*-bidentate.

The pure cobalt complex was characterized by X-ray crystallographic analysis of a single crystal. In this case, however, decomposition of the crystal during analysis resulted in extensive disorder and, therefore, a large error in the data. These problems create some doubt about the ligands bond distances and angles relative to the cobalt(III) center. The largest distortions in terms of non-planarity and fold angles are observed in the *pipdte* ligand, which is clearly under great strain of the folded macrocyclic ligand, due to the involvement of both of its sulphur atoms in the formation of a four-membered ring. Finally, least-squares refinement resulted in R-values somewhat higher than normally obtained for a "good" structure, owing to the poor quality of the data, high thermal motion and disorder associated with several groups. Nevertheless, the material was characterized unambiguously and the essential structural features and bonding modes were established.

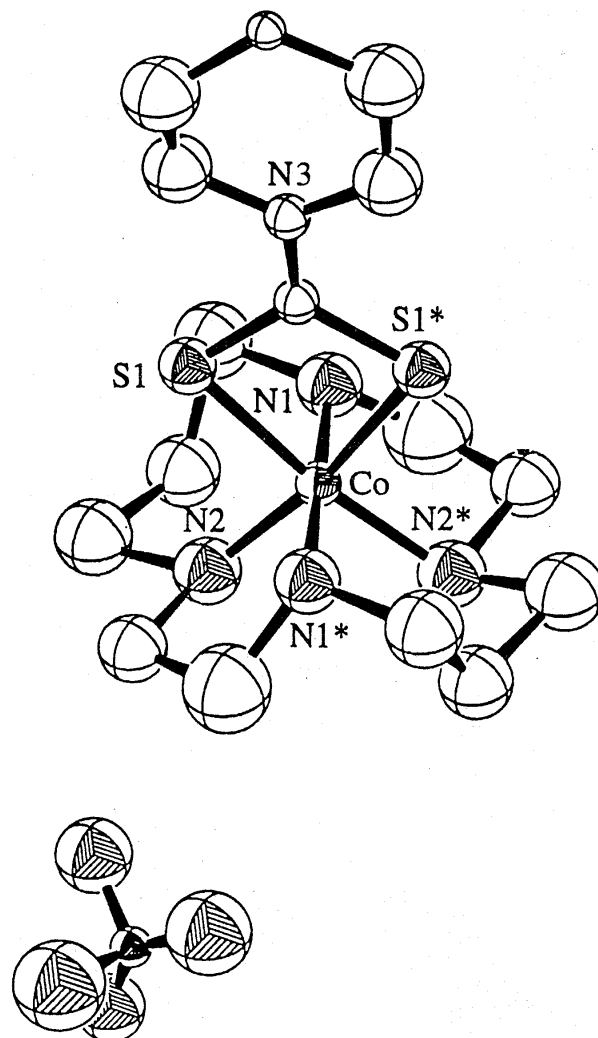


Figure 1. A PLUTO diagram of *cis*-[Co(pipdte)cyclam]<sup>2+</sup> and ClO<sub>4</sub><sup>-</sup> ions

To the best of our knowledge, this structure is the first example of a mixed-ligand complex with a heterocyclic *Rdte*<sup>-</sup> ligand and may be a prototypal structural building block in this area of chemistry.

The unit cell consists of the complex cation, [Co(pipdte)cyclam]<sup>2+</sup>, and ClO<sub>4</sub><sup>-</sup> ions. A PLUTO diagram of these ions is given in Fig.1. Selected inter atomic distances and angles are given in Table 3.

As it can be seen, the cobalt atom is coordinated to the four nitrogen atoms of *cyclam* and to the two sulphur atoms of the heterocyclic piperidine dithiocarbamato ion. The *cyclam* ring configuration is folded, as predicted on the basis of minimum steric constraints [2] and by analogy with the known structure of [Co(X)cyclam]<sup>n+</sup> ions, where X = *en* [16] or *ox* [2]. The five-membered chelate rings of the macrocycle adopt a *gauche*, and the six-membered rings a *chair* conformation. A four-membered ring is formed when

Table 3. Selected bond distances and angles for *cis*-[Co(*pipdtc*)(*cyclam*)](ClO<sub>4</sub>)<sub>2</sub>

Bond distances (Å)		Bond angles (°)			
Co-S1	2.245(5)	S1-Co-S1*	75.7(3)	Co-N1-C2	110.0(1)
Co-N1	1.840(2)	S1-Co-N1	91.3(5)	Co-N1-C3	123.0(1)
Co-N2	2.000(2)	S1-Co-N2	93.0(1)	Co-N2-C1	103.0(1)
N1-C2	1.55(4)	S1*-Co-N1	87.5(5)	Co-N2-C5	130.0(1)
N1-C3	1.70(3)	S1*-Co-N2	95.2(5)	C2-N1-C3	103.0(2)
N2-C1	1.74(3)	N1-Co-N2	88.6(7)	C1-N2-C5	80.0(1)
N3-C6	1.37(2)	N2-Co-N2*	170.9(6)	C3-C4-C5	79.0(5)
C3-C4	1.64(3)	N1-Co-N2*	92.2(8)	N1-C3-C4	87.0(1)
C7-C8	1.40(3)	N1-Co-N1*	178.0(1)	N2-C1-C2	97.0(2)
C8-C9	1.43(2)			S1-C6-S1*	108.0(1)
		O1-Cl-O3	107.0(2)	S1-C6-N3	126.0(5)
Cl-O1	1.28(2)	O1-Cl-O4	111.0(1)	N3-C7-C8	117.0(1)
Cl-O2	1.08(2)	O2-Cl-O3	124.0(2)	C7-C8-C9	119.0(2)
Cl-O3	1.00(3)	O2-Cl-O4	106.0(1)		
Cl-O4	1.29(3)	O3-Cl-O4	95.0(2)		
		Cl-O3-O4	48.0(1)		

both the sulphur donors of the *pipdtc* ligand are coordinated to the central metal ion.

In comparison with ethylenediamine [16] and oxalato [2] complex analogues, the Co-N(*cyclam*) bonds are sparingly different and show that the nitrogen atoms have similar bond-distances depending on chelate-ring formation in the macrocycle. The four Co-N(*cyclam*) bonds are a marginally larger on average. The longer Co-N2(*cyclam*) bond length confirms the relatively weak nature of these bonds. Probably, steric congestion in the folded macrocycle, and the presence of the additional bidentate ligand in the neighborhood of the nitrogen atoms may contribute to this weakening. The N3-C6 bond distance from *pipdtc* is 1.37(2) Å and corresponds to this bond having a partially double character, as is also to be expected in the case of C6-S bond. Consequently, the S-C-S\* distances probably indicate partially double character displaying a double *pipdtc* binding mode. The N-Co-N angle of the five membered ring of *cyclam* [88.6(7)°] is, as expected, smaller than that of the six-membered ones [92.2(8)°]. Within the six-membered rings the Co-N-C angles of 123.0(1) and 130.0(1)° are bigger than the corresponding ones found in the *en* [16] and *ox* [2] analogues structure of the complexes. These differences suggest that the bidentate *Rdtc*<sup>-</sup> ligand has a greater strained structure and the coordination around the central ion is consequently a more distorted octahedron. Further evidence of strain may probably be found in the C-N and C-C bond distances, which tend to be slightly

longer in the six- than in the five-membered rings. This is supported by the fact, that coordination of different bidentate to the central cobalt in the same way causes differences on the ring-size effect and donor atoms. The order *ox* < *en* < *pipdtc* chelate ligands can be recognized as a consequence of the less distortion of the octahedron structure, from five- to four-membered rings. The influence of different donor atoms presented besides nitrogen from *cyclam* as oxygen (oxalato ligand), nitrogen (ethylenediamine) or sulphur (piperidin dithiocarbamate ligand) is reflected too, and could be described to the increasing polarisability in order S > N > O [19].

#### Acknowledgments

We are grateful to Professor Naohide Matsumoto from Department of Chemistry, Kyushu University, Japan for the X-ray analysis. This research was supported by the Ministry of Science and Technology of the Republic Serbia (Project 02E35) and partially by the Federal Ministry for Development, Science and Environment of the FR Yugoslavia (Project OSIO48).

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**IZVOD**PRELIMINARNA STRUKTURA CIS-PIPERIDIN-DITIOKARBAMATO  
(1,4,8,11-TETRA-AZACIKLOTETRADEKAN)KOBALT(III)- PERHLORATA

(Naučni rad)

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Novi kompleks kobalta(III) sa 1,4,8,11-tetraazaciklotetradekanom (*cyclam*) i heterocikličnim ditiokarbamato ligandom, piperidin- ditiokarbamato-S,S\* jonom ispitan je rendgenskom strukturnom analizom. Dobijeni kristali pripadaju monokliničnom sistemu, prostorne grupe C2/c (#15), gde je  $a = 14.342(2)$ ,  $b = 16.596(2)$ ,  $c = 12.151(2)$  Å,  $\beta = 106.430(10)^\circ$ ,  $V = 2774.2(5)$  Å<sup>3</sup>,  $Z = 8$ . Struktura je rešena direktnim metodama i utačnjena metodom najmanjih kvadrata primenom pune matrice za 1566 refleksija ( $I > 3.00\sigma(I)$ ) do  $R = 0.181$  i  $R_w = 0.129$ .

Kompleks piperidin-ditiokarbamato(1,4,8,11-tetraazaciklotetradekan) kobalt(III) – perhlorat, [Co(pipdte)cyclam](ClO<sub>4</sub>)<sub>2</sub> je *cis*-oktaedarske geometrije sa nabranim makrociklom oko centralnog jona kobalta i bidentatno koordinovanim *pipdte* ligandom koji zauzima preostala dva mesta.

Ključne reči: kobalt(III) kompleksi  
• *cyclam* piperidin-ditiokarbamato  
jon • kristalna struktura.  
Key words: Cobalt(III) complexes •  
*cyclam* • Piperidine dithiocarbamate  
ion • Crystal structure •