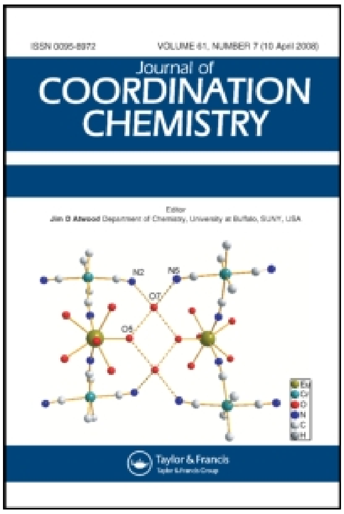

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, spectroscopic characterization and crystal structure of [*trans*-Co(en)$_2$Cl$_2$][*trans*-Co(en)$_2$(S$_2$O$_3$)$_2$]

Raj Pal Sharma[a]; Rajni Sharma[a]; Ritu Bala[a]; Miguel Quiros[b]; Juan M. Salas[b]
[a] Department of Chemistry, Panjab University, Chandigarh 160014, India [b] Departamento de Quimica Inorganica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

To cite this Article Sharma, Raj Pal , Sharma, Rajni , Bala, Ritu , Quiros, Miguel and Salas, Juan M.(2005) 'Synthesis, spectroscopic characterization and crystal structure of [*trans*-Co(en)$_2$Cl$_2$][*trans*-Co(en)$_2$(S$_2$O$_3$)$_2$]', Journal of Coordination Chemistry, 58: 13, 1099 — 1104

To link to this Article: DOI: 10.1080/00958970500138355

URL: http://dx.doi.org/10.1080/00958970500138355

Journal of Coordination Chemistry
Vol. 58, No. 13, 10 September 2005, 1099–1104

Taylor & Francis
Taylor & Francis Group

Synthesis, spectroscopic characterization and crystal structure of [*trans*-$Co(en)_2Cl_2$][*trans*-$Co(en)_2(S_2O_3)_2$]

RAJ PAL SHARMA*†, RAJNI SHARMA†, RITU BALA†,
MIGUEL QUIROS‡ and JUAN M. SALAS‡

†Department of Chemistry, Panjab University, Chandigarh 160014, India
‡Departamento de Quimica Inorganica, Facultad de Ciencias,
Universidad de Granada, 18071 Granada, Spain

(*Received in final form 9 February 2005*)

Trans-[$Co(en)_2(Cl_2)$]Cl reacts with sodium thiosulphate in a 2 : 1 stoichiometric ratio in water to give the unexpected green product [*trans*-$Co(en)_2Cl_2$][*trans*-$Co(en)_2(S_2O_3)_2$] green in almost quantitative yield. This represents the first salt containing [*trans*-$Co(en)_2(S_2O_3)_2$]$^-$. The complex salt crystallizes and is triclinic, space group $P\bar{1}$, with $a = 6.3067(4)$, $b = 7.7820(5)$, $c = 12.7658(8)$ Å, $\alpha = 100.043(1)$, $\beta = 91.562(1)$, $\gamma = 107.339(1)°$, $Z = 1$, $V = 586.80(6)$ Å^3. The structure was refined to $R_1 = 0.0199$ and $wR_2 = 0.0537$.

Keywords: Cobalt(III); 1,2-Diaminoethane; Thiosulphate; Crystal structure; Spectroscopy

1. Introduction

We are focused on a program aimed at exploiting cobaltammines for molecular recognition of various anions and have reported [1–7] the interaction of [*cis*-$Co(en)_2(N_3)_2$]$^+$, [$Co(NH_3)_6$]$^+$ and [*trans*-$Co(en)_2Cl_2$]Cl (en = 1,2-diaminoethane) with various organic and inorganic anions. Prompted by these studies, we undertook a study of the reaction of [*trans*-$Co(en)_2Cl_2$]Cl with thiosulphate. The thiosulphate ion shows a variety of bonding modes in its metal complexes and salts, ranging from ionic to coordination as a monodentate via sulfur [8] or oxygen atom [9] or a bridging bidentate [10]. In an attempted synthesis of the thiosulphate salt of the *trans* cation, an unprecedented product, [*trans*-$Co(en)_2Cl_2$][*trans*-[$Co(en)_2(S_2O_3)_2$], was obtained. This has been characterized spectroscopically and by a single-crystal X-ray structure determination. The structure represents the first example of solid state characterization of the [*trans*-$Co(en)_2(S_2O_3)_2$]$^-$ anion.

---

*Corresponding author. Email: rpsharmapu@yahoo.co.in

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2005 Taylor & Francis Group Ltd
DOI: 10.1080/00958970500138355

2. Experimental

Analytical grade reagents were used without any further purification. [*Trans*-Co(en)$_2$Cl$_2$]Cl was prepared according to a literature method [11]. Cobalt was determined by a standard method [12] and C, H, N were estimated using a Perkin-Elmer 2400 elemental analyser. IR spectra were recorded with a Perkin-Elmer RX FTIR spectrophotometer using KBr plates. Electronic spectra were recorded using a Hitachi 330 spectrophotometer with H_2O as solvent.

2.1. [trans-*Co(en)*$_2$*Cl*$_2$][trans-*Co(en)*$_2$*(S*$_2$*O*$_3$*)*$_2$]

A solution of [*trans*-Co(en)$_2$Cl$_2$]C1 (1.0 g, 0.002 mol) in 25 cm^3 of water was mixed with a solution of $Na_2S_2O_3 \cdot 5H_2O$ (0.43 g, 0.001 mol) in 20 cm^3 of water at room temperature. Green crystals of [*trans*-Co(en)$_2$Cl$_2$][*trans*-Co(en)$_2$(S$_2$O$_3$)$_2$], which appeared within 30 min, were collected and air-dried (yield 80%; m.p. >200°C). Anal. Calcd for $C_8H_{32}C_{12}Co_2N_8O_6S_4$ (%):C, 14.7; H, 4.9; N, 17.1; Co, 18.0. Found: C, 15.2; H, 4.6; N, 17.4; Co, 18.1. The complex is soluble in water, freely soluble in DMSO and is stable in air.

2.2. *Crystallography*

Intensity data for a crystal with dimensions 0.34 × 0.32 × 0.12 mm were measured at room temperature on a Bruker Smart Apex CCD diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å), such that $\theta_{\max}$ was 28.25°. A total of 1687 reflections were processed. The structure was solved using the SHELX-97 program [13] and refined by a full-matrix least-squares procedure based on F^2. A summary of crystallographic data is given in table 1 and final fractional atomic coordinates are listed in table 2. Selected interatomic parameters are given in table 3 and the numbering scheme employed is shown in figure 1, drawn using Xtal_GX [14]. Full lists of crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC No. 234731); see http:/www.rsc.org/suppdata for crystallographic data in cif format.

3. Results and discussion

3.1. *Synthesis and spectroscopy*

[*Trans*-Co(en)$_2$Cl$_2$]Cl and sodium thiosulphate were reacted in a 2 : 1 molar ratio in water with the expectation that [*trans*-Co(en$_2$)Cl$_2$]$_2$S$_2$O$_3$ would be obtained. However, the reaction proceeded in an altogether different manner to give a green crystalline product of quite different stoichiometry. On the basis of elemental analysis, the formula [*trans*-Co(en)$_2$Cl$_2$][*trans*-Co(en)$_2$(S$_2$O$_3$)$_2$] could be proposed. Infrared spectrum of the new salt has been tentatively assigned on the basis of earlier reports in the literature [15]. The band at 889 cm^{-1} is assigned to CH_2 rocking and that at 1574 cm^{-1} to δNH_2 [16]. Coordination of thiosulphate has been studied extensively by IR spectroscopy and, according to Freedman and Straughan [9], $\nu_a(SO_3)$ near 1130 cm^{-1} is diagnostically most useful (>1175: *S*-bridging; 1175–1130,

Table 1. Crystal data and structure refinement details for $[trans\text{-Co(en)}_2\text{Cl}_2][trans\text{-Co(en)}_2(\text{S}_2\text{O}_3)_2]$.

Empirical formula	$C_8H_{32}Cl_2Co_2N_8O_6S_4$
Formula weight	653.42
Space group	Triclinic, $P\bar{1}$
Unit cell dimensions	$a = 6.3067(4)$ Å $\alpha = 100.043(1)^\circ$
	$b = 7.7820(5)$ Å $\beta = 91.562(1)^\circ$
	$c = 12.7658(8)$ Å $\gamma = 107.339(1)^\circ$
V	586.80(6) $Å^3$
Z	1
Calculated density	1.849 $Mg\,m^{-3}$
Absorption coefficient	2.040 mm^{-1}
$F(000)$	336
Crystal size	0.34 × 0.32 × 0.12 mm
θ range for data collection	1.63 to 23.27°
Limiting indices	$-6 \le h \le 7$, $-8 \le k \le 8$, $-14 \le l \le 14$
Reflections collected/unique	4977/1687 [R(int) = 0.0140]
Completeness to $\theta = 23.27^\circ$	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7919 and 0.6052
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.3P]$ where $P = (F_o^2 + 2F_o^2)/3$
Data/Restraints/Parameters	1687/0/139
Goodness-of-fit on F^2	1.082
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0199$, $wR2 = 0.0537$
R indices (all data)	$R1 = 0.0203$, $wR2 = 0.0539$
Largest diff. peak and hole	0.344 and -0.286 e $Å^{-3}$

Table 2. Atomic coordinates (Co, Cl, S, × 10^5; others × 10^4) and equivalent isotropic displacement parameters (Å × 10^4) in $[trans\text{-Co(en)}_2\text{Cl}_2][trans\text{-Co(en)}_2(\text{S}_2\text{O}_3)_2]$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Co(1)	50000	0	50000	229(1)
Cl	19410(9)	−7579(8)	38744(4)	378(2)
N(1)	4209(3)	−2540(2)	5224(1)	326(4)
C(1)	2308(4)	−2873(3)	5897(2)	430(6)
C(2)	2738(4)	−1176(3)	6744(2)	414(6)
N(2)	3257(3)	420(2)	6204(1)	291(4)
Co(2)	0	50000	0	216(1)
S(1)	2512(8)	44871(7)	17265(4)	286(2)
S(2)	34270(8)	45443(7)	21612(4)	259(1)
O(1T)	3416(3)	4327(2)	3265(1)	377(4)
O(2T)	4971(2)	6323(2)	2038(1)	354(4)
O(3T)	3922(3)	3060(2)	1441(1)	385(4)
N(3)	2841(3)	6983(2)	204(1)	291(4)
C(3)	2433(4)	8784(3)	434(2)	378(5)
C(4)	480(4)	8577(3)	1102(2)	376(5)
N(4)	−1324(3)	6923(2)	569(1)	291(4)

S-coordination; 1130, ionic S_2O_3; < 1130 cm^{-1}, *O*-coordination). On the basis of this criterion, the bands at 1141 and 1160 cm^{-1} assigned to $\nu_a(SO_3)$ in $S_2O_3^{-2}$ confirm that thiosulphate is an *S*-bonded unidentate in the present complex salt. The band at 428 cm^{-1} is assigned to the Co–N stretch.

The electronic spectrum of the salt has been recorded in H_2O. It shows absorption at 604 nm (shoulder), strong absorptions at 542 and 333 nm, and an intense absorption

Table 3. Selected bond lengths [Å] and angles [°] for [*trans*-$Co(en)_2Cl_2$][*trans*-$Co(en)_2(S_2O_3)_2$].

Co(1)–N(2)	1.9515(16)	N(2)–Co(1)–N(1)	85.73(7)
Co(1)–N(1)	1.9635(17)	N(2)–Co(1)–Cl	90.10(5)
Co(1)–Cl	2.2382(5)	N(1)–Co(1)–Cl	89.71(6)
N(1)–C(1)	1.480(3)	C(1)–N(1)–Co(1)	108.89(14)
C(1)–C(2)	1.503(3)	N(1)–C(1)–C(2)	106.58(19)
C(2)–N(2)	1.481(3)	N(2)–C(2)–C(1)	107.65(18)
Co(2)–N(3)	1.9610(17)	C(2)–N(2)–Co(1)	109.52(13)
Co(2)–N(4)	1.9651(17)	N(3)–Co(2)–N(4)	85.61(7)
Co(2)–S(1)	2.3168(5)	N(3)–Co(2)–S(1)	93.80(5)
S(1)–S(2)	2.0492(7)	N(4)–Co(2)–S(1)	87.20(5)
S(2)–O(1T)	1.4487(15)	S(2)–S(1)–Co(2)	110.43(3)
S(2)–O(3T)	1.4618(15)	O(1T)–S(2)–O(3T)	113.49(9)
S(2)–O(2T)	1.4727(16)	O(1T)–S(2)–O(2T)	111.80(9)
N(3)–C(3)	1.480(3)	O(3T)–S(2)–O(2T)	109.76(10)
C(3)–C(4)	1.503(3)	O(1T)–S(2)–S(1)	105.45(7)
C(4)–N(4)	1.481(3)	O(3T)–S(2)–S(1)	107.76(7)
		O(2T)–S(2)–S(1)	108.29(7)
		C(3)–N(3)–Co(2)	110.00(13)
		N(3)–C(3)–C(4)	107.22(18)
		N(4)–C(4)–C(3)	107.68(18)
		C(4)–N(4)–Co(2)	108.76(13)

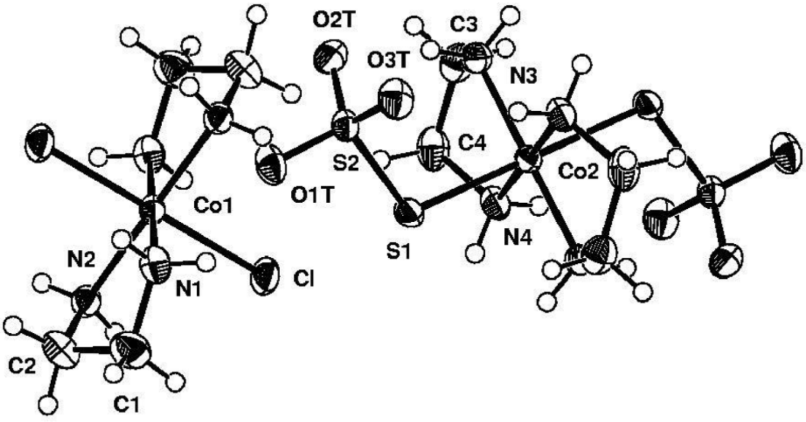

Figure 1. ORTEP drawing of [*trans*-$Co(en)_2Cl_2$][*trans*-$Co(en)_2(S_2O_3)_2$] showing the atom numbering scheme.

band at 242 nm. The spectrum is thus consistent with that previously reported [17, 18] for [*trans*-$Co(en)_2(S_2O_3)_2$]$^-$. The peak at 242 nm has been assigned to ligand-to-metal charge transfer, and characteristically arises whenever sulfur is coordinated to cobalt(III) [19–21].

3.2. *X-ray crystallography*

The structure of the salt has been unambiguously determined by single-crystal X-ray crystallography. Although both *cis* and *trans* isomers of [$Co(en)_2(S_2O_3)_2$]$^-$ anion are known in the literature, this is the first X-ray structure report confirming the existence of [*trans*-$Co(en)_2(S_2O_3)_2$]$^-$, earlier attempts at structural characterization having failed [20]. The structure reveals the presence of a discrete $[Co(en)_2(Cl_2)]^+$ cation and $[Co(en)_2(S_2O_3)_2]^-$ anion. Cobalt atoms are placed at crystallographic inversion centres and so the geometry is *trans* for both. In the anion, two thiosulphate ligands bond through sulphur. Bond lengths and angles for cation in the title salt are comparable to those of [*trans*-$Co(en)_2Cl_2$]Cl [22], but differences, as compared to the structure of [*trans*-$Co(en)_2Cl_2$][$CoCl_4$] [23], indicate that the presence of a different anion affects the Co–N bond length in the cation considerably; other bond lengths remain unaffected.

Significant bond lengths in the anion are Co–N 1.9630(17), C–N 1.4800(3), C–C 1.5031(3), Co–S 2.3168(5), S–S 2.0492(7) and S–O 1.4610(15) Å. Corresponding values [24] in [*trans*-$Co(en)_2(NCS)(S_2O_3)$] · H_2O are 1.964(7), 1.484(10), 1.4995(15), 2.246(3), 2.052(4) and 1.462(7) Å and in $[Co(NH_3)_5(S_2O_3)]Cl \cdot H_2O$ [25] are Co–S 2.287(1), S–S 2.048(2), S–O 1.463(3) Å. Bond angles in the anion of the present salt, C–C–N 107.40(18), N–Co–N 85.61(7), N–Co–S 90.5(5), C–N–Co 109.00(13), O–S–O 111.68(9), O–S–S 107.16(7), S–S–Co 110.43(3)°, may be compared to those in *trans*-[$Co(en)_2(NCS)(S_2O_3)$] · H_2O, these being 107.71(7), 89.62(3), 88.71(2), 108.37(5), 112.38(3), 105.5(3), 113.7(1)°, respectively. Related angles in $[Co(NH_3)_5(S_2O_3)]Cl \cdot H_2O$ are O–S–O 111.2(1), O–S–S 106.5(1), S–S–Co 110.20(6)°.

The crystal lattice of the present salt is stabilized by an intricate network of N–H ··· O hydrogen bonds. Significant hydrogen bond distances are N1 ··· O1T (x, $y-1$, z) 3.086(2), N1 ··· O1T ($1-x$, $-y$, $1-z$) 3.149(3), N2 ··· O2T ($1-x$, $1-y$, $1-z$) 2.983(2), N3 ··· O3T ($1-x$, $1-y$, $-z$) 2.972(2), N4 ··· O3T ($-x$, $1-y$, $-z$) 3.011(2) and N4 ··· O2T ($x-1$, y, z) 3.016(2) Å. The structure must be additionally stabilized by the coulombic forces of attraction between counterions.

Acknowledgements

The authors gratefully acknowledge the financial support of the UGC through grant F.12-38/2003 (SR).

References

[1] R.P. Sharma, R. Sharma, R. Bala, M. Quiros, J.M. Salas. *J. Coord. Chem.*, **56**, 1581 (2003).
[2] R.P. Sharma, R. Bala, R. Sharma, K.K. Bhasin, R.K.Chadha. *J. Coord. Chem.*, **57**, 313 (2004).
[3] R.P. Sharma, R. Bala, R. Sharma, P. Venugopalan. *J. Mol. Struct.*, **694**, 229 (2004).
[4] R.P. Sharma, R. Bala, R. Sharma, P. Venugopalan. *J. Coord. Chem.*, **57**, 1563 (2004).
[5] R.P. Sharma, R. Bala, R. Sharma, M. Quiros, J.M. Salas. *J. Coord. Chem.*, **58**, 217 (2005).
[6] R.P. Sharma, R. Bala, R. Sharma, B.K. Vermani, D.S. Gill, P. Venugopalan. *J. Coord. Chem.* **58**, 309 (2005).
[7] R.P. Sharma, R. Sharma, R. Bala, P. Venugopalan. *J. Chem. Crystallogr.* (In press).
[8] M.E. Kastner, D.A. Smith, A.G. Kuzmission, J.N. Cooper, T. Tyree, M. Yearick. *Inorg. Chim. Acta*, **158**, 185 (1989).
[9] A.N. Freedman, B.P. Straughan. *Spectrochim. Acta A*, **27**, 1455 (1971).
[10] J.N. Cooper, D.S. Buck, M.G. Katz, E.A. Deutsch. *Inorg. Chem.*, **19**, 3856 (1980).
[11] J.C. Bailar Jr. *Inorg. Synth.*, **2**, 222 (1946).
[12] A.I. Vogel. *A Textbook of Quantitative Inorganic Analysis*, Longmans, London (1961).
[13] G.M. Sheldrick. *SHELXL97 and SHELXS97*, University of Göttingen, Germany (1997).
[14] S.R. Hall, D. du Boulay. *Xtal_GX*, University of Western Australia, Perth (1997).
[15] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th Edn, John Wiley and Sons, New York (1997).

[16] J. Chatt, L.A. Duncanson, B.M. Gatehouse, J. Lewis, R.S. Nyholm, M.L. Tobe, L.M. Venanzi, P.F. Todd. *J. Chem. Soc.*, 4073 (1959).
[17] K. Akamatsu, J. Hidaka, Y. Shimura. *Bull. Chem. Soc. Jpn.*, **50**, 533 (1977).
[18] J. Hidaka, J. Fujita, Y. Shimura, R. Tsuchida. *Bull. Chem. Soc. Jpn.*, **32**, 1317 (1959).
[19] M.J. Heeg, R.C. Elder, E. Deutsch. *Inorg. Chem.*, **18**, 2036 (1979).
[20] J.N. Cooper, J.D. McCoy, M.G. Katz, E. Deutsch. *Inorg. Chem.*, **19**, 2265 (1980).
[21] C.J. Weschler, E. Deutsch. *Inorg. Chem.*, **12**, 2682 (1973).
[22] K.A. Becker, G. Grosse, K. Plieth. *Z. Kristallogr.*, **112**, 375 (1959).
[23] U. Schubert, B. Zimmmer-Gasser, K.C. Dash, G.R. Chaudhury. *Cryst. Struct. Comm.*, **1**, 239 (1981).
[24] K. Tang, M.E. Kastner, J.N. Cooper, M. Kanaskie, A. Monoski. *Acta Cryst.*, **C49**, 1265 (1993).
[25] R.J. Restivo, G. Ferguson, R.J. Balahura. *Inorg. Chem.*, **16**, 167 (1977).