Optically Active *cis*-Dianiono(tetraamine)chromium-(III) Complexes. VI. Chiroptical Properties of *cis*-[Cr(NCS)$_2$(tet *b*)]-NCS – Extreme Solvent Dependence

A. WATSON and D. A. HOUSE*

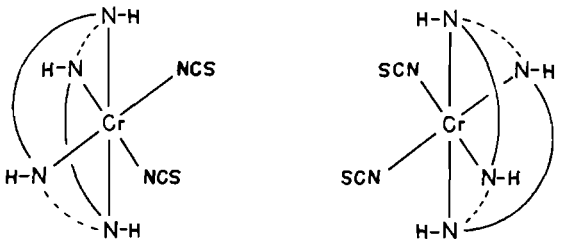
Chemistry Department, University of Canterbury, Christchurch, New Zealand

Received October 3, 1984

Cis-[Cr(NCS)$_2$(tet *b*)]NCS** has been resolved with potassium antimony-(+)-tartrate to give both diastereoisomerides and these have been converted back to the enantiomeric thiocyanate salts. The ORD and CD spectra of the thiocyanate salt from the less soluble diastereoisomeride have been recorded in 12 different solvents at room temperature. The sign of rotation at the sodium D lines (589 nm) varies from −461 in DMF to +564° M^{-1} m^{-1} in THF, with only a 5% variation in the intensity of the visible absorption maxima at 530 nm, over all solvents. This enantiomer is characterised by a positive CD (50% intensity variation over all solvents) at 485 nm and a negative CD at 380 nm (50% intensity variation with solvent), but at 530 nm, the CD intensity varies from −0.290 (py) to +0.188 M^{-1} cm^{-1} (dioxane). This extreme solvent variation is attributed to a change in ring pair dominance.

Tet *a* and tet *b* are the meso and racemic macrocyclic ligands formed by reduction of the condensation product of 1,2-ethanediamine monohydrobromide and acetone [1]. The racemic form, tet *b*, has been resolved via the Ni(II) complex [2, 3] but other transition metal complexes with the (RR) or (SS) forms are not well characterised.

Racemic tet *b* forms a most unusual series of *cis*-dianionochromium(III) complexes [4, 5] and single crystal X-ray structures of salts of Cr(CO$_3$)(tet *b*)$^+$ and *cis*-Cr(OH)$_2$(tet *b*)$^+$ have been determined [5, 6].



I
sec-NH (SSSS), C(RR), Δ_{tn}, Λ_{en}.

II
sec-NH (RRRR), C(SS), Λ_{tn}, Δ_{en}.

Fig. 1. Optical isomers of *cis*-Cr(NCS)$_2$(tet *b*)$^+$ (methyl groups omitted). Note that the R and S assignments for the *sec*-NH protons are reversed from those in an identical environment in *cis*-cyclam complexes, due to the methyl substituents on the six-membered ring changing the priority order of groups attached to the N atom. Five-membered rings are dashed.

In both cases, the sec-NH protons on the 'planar' component of the coordinated macrocycle, point away from the coordinated aniono ligands (Fig. 1).

The stereochemically rigid *cis*-configuration adopted by the CrX$_2$(tet *b*)$^{n+}$ cations makes these complexes ideal models for resolution and we have been successful in separating the diisothiocyanato [4] into enantiomeric forms. There are, however, considerable problems with the assignment of the absolute configuration in *cis*- complexes containing macrocyclic ligands of this type. In particular, the conventional assignment of Λ and Δ have no meaning, as in each enantiomer, the 5- and 6-membered ring pairs are of opposite helicity.

Resolution of *cis*-CrX$_2$(tet *b*)$^{n+}$ complexes will also result in the resolution of the chiral C(5, 12) centers, as the crystal structures of both the X = OH and 2X = CO$_3$ complexes show the racemic cations to consist of equal amounts of the *sec*-NH(SSSS), C(RR) and *sec*-NH(RRRR), C(SS) forms (Fig. 1) [5, 6]. The dinuclear octahedral Ni(II) complex (−)-[{Ni(SS-tet *b*)}$_2$(*d*-tart)(OH$_2$)]$^{2+}$ and *cis*-Ni(SS-tet *b*)(OH$_2$)$_2^{2+}$ also have the *sec*-NH-(RRRR), C(SS) stereochemistry [2, 7].

Thus, the observed CD spectrum for chiral *cis*-CrX$_2$(tet *b*)$^{n+}$ complexes will contain contributions from the chiral carbon centers, as well as depending on which set of chelate ring pairs dominates.

Traditionally, an optically active coordination complex is characterized by the sign of rotation at the Na$_D$ lines (589 nm), *e.g.* (+)-Co(en)$_3^{3+}$. The enantiomeric form will be characterized by the opposite sign, *viz.* (−)-Co(en)$_3^{3+}$ [8]. To be meaningful, these rotation signs are assumed to be solvent invarient and almost temperature invariant at temperatures close to ambient [9]. Certainly, for

*Author to whom correspondence should be addressed.

**Abbreviations used: tet *b* = (RR), (SS)-C(5,12)-5,7,7,12, 14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, tet *a* = (R, S)C(5,12)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, cyclam = 1,4,8,11-tetraazacyclotetradecane, en = $NH_2(CH_2)_2NH_2$, tn = $NH_2(CH_2)_3NH_2$, tnentn = 3,2,3-tet = $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$, entnen = 2,3,2-tet = $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$, DMF = dimethylformamide, DMSO = dimethylsulphoxide, HMPA = hexamethylphosphoramide, EGME = ethyleneglycolmonomethylether = 2-methoxyethanol, THF = tetrahydrofuran, EtAc = ethylacetate, KSbOT = potassium antimony-(+)-tartrate, *d*-tart = (+)-tartrate ion.

0020-1693/85/$3.30

many coordination compounds this is indeed the case, but solvent dependent chiroptical parameters have also been observed [10–14]. Indeed, for *trans*-(RR)-Co(tnentn)$(N_3)_2^+$, the CD spectrum in water is almost enantiomeric with that recorded in DMSO [11].

In this paper we describe the chiroptical properties of optically active *cis*-[Cr(NCS)$_2$(tet *b*)]NCS, where the extreme solvent dependence of a particular enantiomer requires that the solvent be specified to allow the sign of rotation at Na_D to have any relevance.

Experimental

Racemic *cis*-[Cr(NCS)$_2$(tet *b*)]NCS was synthesised as previously described [4], using 5 g of *cis*-[$CrCl_2$(tet *b*)]Cl [4, 5]. The complex was resolved using the method described for *cis*-[Cr(NCS)$_2$-(en)$_2$]NCS [15].

The complex (5 g) was dissolved in a hot solution of 50:50 acetone:water (300 ml) and a hot aqueous solution of KSbOT (5 g, 100 ml) was rapidly added with stirring. The less soluble diastereoisomeride commenced to precipitate immediately, the heat was removed, and the solution allowed to cool in air for 5 min, before filtration (4 g). The more soluble diastereoisomeride (2.3 g) slowly deposited from the mother liquor overnight at room temperature. Both diastereoisomerides were washed successively with water, 2-propanol and then ether, and air dried. These were not characterised further, but converted back to the thiocyanate salts as follows. The SbOT salt (4 g) was stirred with 50 ml of hot acetone and 150 ml of hot water containing 8 g of KCNS was poured in. The product that deposited from the cool solution (2.5 g) was collected, washed with water and then ether. This procedure was repeated, to give 2.5 g of optically pure $(-)_{DMF}$-[Cr(NCS)$_2$(tet *b*)]NCS from the less soluble SbOT salt and 1.5 g of 64% optically pure $(+)_{DMF}$-enantiomer from the more soluble SbOT salt, both as flat glistening maroon needles. *Anal.*: $(-)_{DMF}$-[Cr(NCS)$_2$(tet *b*)]NCS·H_2O, $C_{19}H_{38}CrN_7S_3O$: Calcd. C, 43.16; H, 7.24; N, 18.54%. Found: C, 43.54; H, 7.60; N, 18.53%. Circular dichroism (CD) and optical rotatory dispersion (ORD) spectra were measured using a JASCO-ORD/CD-5 recording spectropolarimeter. Visible absorption spectra were measured in matched 1 cm cells using a Varian DMS-100 recording spectrophotometer.

TABLE I. Solvent Dependence on CD Parameters (−)DMF-*cis*-[Cr(NCS)$_2$(tet *b*)]NCS.

Solvent	λ_{max}[a] (nm)	ϵ (M^{-1} cm^{-1})		λ (nm)	($\Delta\epsilon$) (M^{-1} cm^{-1})				
DMF	528.6	207.3	600	572	534	505	485	477	380
			(+0.038)	(0)	(−0.223)	(0)	(+0.194)	(0)	(−0.417)
HMPA	534.8	219.4	575	544	518	485	469	451	376
			(+0.288)	(0)	(−0.265)	(0)	(+0.034)	(0)	(−0.192)
DMSO	527.7	227.1	584	574	530	501	484	445	378
			(+0.014)	(0)	(−0.260)	(0)	(+0.16)	(0)	(−0.398)
CH_3CN	527.7	205.1	578	548	528	510	482	446	378
			(+0.105)	(0)	(−0.068)	(0)	(+0.263)	(0)	(−0.521)
PY	530.5	210.0	585	567	520	482	470	455	375
			(+0.049)	(0)	(−0.273)	(0)	(+0.021)	(0)	(−0.322)
CH_3NO_2	526.8	218.2	585	560	539	518	485	444	
			(+0.047)	(0)	(−0.084)	(0)	(+0.364)	(0)	
$(CH_3)_3PO_4$	525.9	210.5	577	553	538	524	485	441	377
			(+0.079)	(0)	(−0.063)	(0)	(+0.396)	(0)	(−0.518)
50:50	532.2	215.9	596	575	538	518	482	439	376
DMF:H_2O			(+0.025)	(0)	(−0.223)	(0)	(+0.593)	(0)	(−0.639)
Acetone	528.6	217.2	554	530	488	445	418sh	378	
			(+0.173)	(+0.119)	(+0.347)	(0)	(−0.243)	(−0.545)	
EGME	530.3	209.7	575	533	491	447		380	
			(+0.177)	(+0.052)	(+0.332)	(0)		(−0.523)	
EtAc	530.3	204.8	550sh		491	445		376	
			(+0.222)		(+0.412)	(0)		(−0.493)	
Dioxane	533.0	210.4	553	506	490	444		369	
			(+0.344)	(+0.169)	(+0.188)	(0)		(−0.344)	
THF	532.1	208.1	563	516	492	540		377	
			(+0.320)	(+0.084)	(+0.187)	(0)		(−0.438)	

[a]A second maxima occurs at ~390 nm.

TABLE II. Solvent Dependence on ORD Parameters (−)DMF-*cis*-[Cr(NCS)$_2$(tet *b*)]NCS.

Solvent (DN)[a]		$[M]_D$ (° M^{-1} m^{-1})			λ (nm)	($[M_D]$) (° M^{-1} m^{-1})							
DMF	(27)	−461	562	529	510	494	435	367					
			(−704)	(0)	(+340)	(0)	(−1120)	(−146)					
HMPA	(38.8)	−366	546		500		400sh						
			(−1550)		(−282)		(−1490)						
DMSO	(29.8)	−304	560		530	504	484	431	381	360			
			(−580)		(0)	(+580)	(0)	(−718)	(0)	(+663)			
CH_3CN	(14.1)	−210	553	514	505	499	435	371	363	354			
			(−605)	(0)	(+52.6)	(0)	(−1420)	(0)	(+131)	(0)			
PY	(33.1)	−122	555	530	502		450		360				
			(−437)	(0)	(+700)		(+105)		(+1120)				
CH_3NO_2	(2.7)	+79.2	616	578	560	548	506	487	442	393			
			(+158)	(0)	(−106)	(0)	(+660)	(0)	(−976)	(0)			
$(CH_3)_3PO_4$	(~23)[b]	+105	616	578	555	542	508	487	440	381	355		
			(+132)	(0)	(−158)	(0)	(+660)	(0)	(−1110)	(0)	(+1215)		
DMF:H_2O	(~18)[c]	+144	630	566	512	481	440	395	352				
			(+323)	(+36)	(+1620)	(0)	(−1080)	(0)	(+2260)				
Acetone	(17)	+272	600	562	547	524	510	502	448	392sh	369	361	
			(+297)	(0)	(−124)	(0)	(+52)	(0)	(−1300)	(−650)	(0)	(+780)	
EGME	(~19)[d]	+332	610	566	552	538	510	494	455	402			
			(+369)	(0)	(−147)	(0)	(+369)	(0)	(−737)	(0)			
EtAc	(?)	+418	596	520	450	381	363						
			(+433)	(0)	(−1330)	(0)	(+785)						
Dioxane	(14.8)	+455	600	566	528	504			454	378	366		
			(+471)	(0)	(−714)	(−519)			(−942)	(0)	(+260)		
THF	(20)	+564	600	566	534	505			450	368	366		
			(+566)	(0)	(−541)	(−221)			(−737)	(0)	(+615)		

[a]Gutmann 'donor number', ref. 19. [b]Value for $(Bu)_3PO_4$. [c]Value for water. [d]Value for EtOH.

Results and Discussion

The CD, ORD and visible absorption spectra of $(-)_{DMF}$-*cis*-$[Cr(NCS)_2(tet\ b)]NCS$ derived from the less soluble SbOT salt were recorded in twelve solvents at room temperature and the chiroptical parameters are listed in Tables I and II.

The sign of rotation at 589 nm varies from −461 in DMF to +564° M^{-1} m^{-1} in THF, with only a 5% variation in the intensity of the visible absorption maxima at 530 nm over all solvents. This enantiomer is characterised by a positive CD (50% intensity variation over all solvents) at 485 nm and a negative CD at 380 nm (50% intensity variation with solvent). At 530 nm the CD intensity varies from −0.290 (py) to +0.188 M^{-1} cm^{-1} (dioxane). The order of solvent effect on $[M]_D$ is: DMF < HMPA < DMSO < MeCN < py < $MeNO_2$ < Me_3PO_4 < Me_2CO < EGME < EtAc < dioxane < TMF (Table II). Closer inspection of the ORD curves (Fig. 2) show that for the first six solvents (DMF-py), the Cotton effect under the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition (530 nm) is negative, whereas for the remainder ($MeNO_2$THF), a positive Cotton effect is observed. We have argued previously, that for *cis*-$Cr(en)_2X_2^{n+}$ (X ≠ halogen) complexes, a positive Cotton effect in this region is characteristic of the Λ absolute configuration [16]. If this empirical rule can be extended to *cis*-$Cr(tn)_2X_2^{n+}$ systems, we suggest that the solvent dependent ORD and CD spectra observed here are due to a change in ring pair dominance with a Δ configuration in strongly donating solvents.

The factors determining which ring pair will dominate are subtle. The CD spectrum (in aqueous acid) of (−)-(RRRR)-*cis*-$CrCl_2$(cyclam)$^+$ * (Fig. 1) indicates a Δ absolute configuration with the tn rings dominant, whereas its precursor, (−)-(RRRR)-Cr(ox)(cyclam)$^+$ has a CD spectrum characteristic of a Λ configuration with the en rings dominant. Thus, small changes in non-bonded interactions can bring about a change in ring dominance and such changes could easily occur by solvation.

Previous workers [10, 14] have attributed solvent effects of this type to specific N–H-solvent hydrogen bonds. In particular, ^1H NMR studies suggest that it is the equatorial N–H groups that are stereoselectively solvated, giving rise to a chiral nitrogen center that contributes to the nett chirality. Previously studied complexes *e.g.* (+)-*trans***-$CoCl_2$(R-pn)$_2^+$ [14] and Λ-*cis* $Co(NCS)_2(en)_2^+$ [10] have both axial and equatorial N–H protons which can be solvated, and if solvation were equal, no induced chirality would result. However, if the equatorial N–H group is stereoselectively solvated the prochiral N center acquires the same configuration as (S)-N-methyl-(R)-propane-1,2-diamine [14] or (S)-N-methyl-1,2-ethanediamine, with the methyl group in the equatorial orientation.

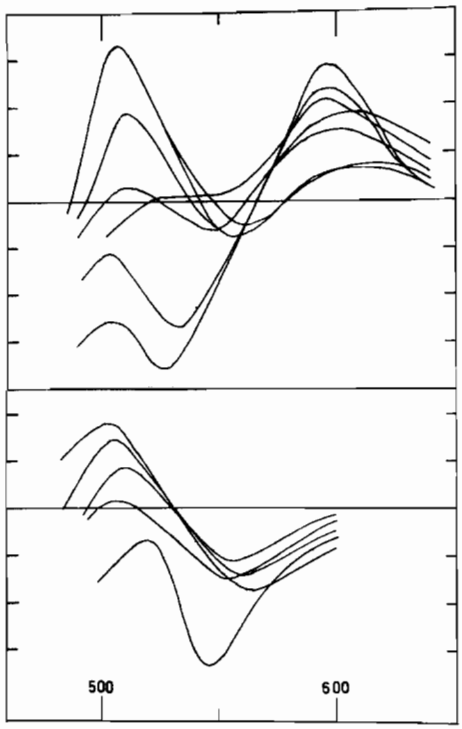


Fig. 2. ORD spectra of $(-)_{DMF}$-$Cr(NCS)_2(tet\ b)^+$ in various solvents. Reading downwards at 500 nm the solvents are CH_3NO_2 = $(CH_3)_3PO_4$, EGME, acetone, EtAc, THF, dioxane, py, DMSO, DMF, CH_3CN, HMPA. For the upper set (CH_3NO_2–dioxane), each ordinate division corresponds to ±200° M^{-1} m^{-1}, and for the lower set (py–HMPA) to ±400° M^{-1} m^{-1}.

The present complex, *cis*-$Cr(NCS)_2(tet\ b)^+$ has only equatorial *sec*-NH protons and strong solvation appears to result in a change in ring pair dominance. On the basis of our discussion of the CrX_2(cyclam)$^+$ system, we have suggested that if X is a monodentate ligand, then the 6-membered tn rings will dominate. If this is the case, then a Λ_{tn} configuration in weakly donating solvents implies an (RRRR)-*sec*-NH configuration (with C(SS)) for the less soluble SbOT salt of $(-)_{DMF}$-$Cr(NCS)_2(tet\ b)^+$. (Figs. 1, 2).

Acknowledgements

We thank the University Grants Committee for providing funds to purchase instruments used in this research and the University of Canterbury for research grant 591695.

*The absolute configuration of (−)-(RRRR)-*cis*-$[CrCl_2(cyclam)]ClO_4$ has been determined by a single crystal X-ray structure [17].

**Presumably the *trans*-Me-*trans*-$CoCl_2(R\text{-}pn)_2^+$ isomer [18].

References

1 R. W. Hay, G. A. Lawrence and N. F. Curtis, *J. Chem. Soc., Perkin Trans. 1,* 591 (1975).
2 H. Ito, J. Fujita, K. Toriumi and T. Ito, *Bull. Chem. Soc. Jpn., 54,* 2988 (1981).
3 M. Wermeille, E. Sledziewska and K. Bernauer, *Helv. Chim. Acta, 57,* 180 (1974).
4 D. A. House, R. W. Hay and M. Akbar Ali, *Inorg. Chim. Acta, 72,* 239 (1982).
5 J. Eriksen and O. Mønsted, *Acta Chem. Scand., Ser. A:, 37,* 579 (1983).
6 E. Bang and O. Mønsted, *Proc. I.C.C.C., 22,* 407 (1982); *Acta Chem. Scand., Part A:, 38,* 281 (1984).
7 H. Ito, M. Sugimoto and T. Ito, *Bull. Chem. Soc. Jpn., 55,* 1971 (1982).
8 K. F. Purcell and J. C. Kotz, 'Inorganic Chemistry', Saunders, 1977, p. 638.
9 F. Woldbye, *Proc. R. Soc. London, Ser. A:, 297,* 79 (1967).
10 U. Sakaguchi, H. Nazakawa, K. Saki and H. Yoneda, *Bull. Chem. Soc. Jpn., 55,* 1862 (1982).
11 B. Bosnich and J. MacB. Harrowfield, *J. Am. Chem. Soc., 94,* 989 (1972).
12 B. Bosnich and J. MacB. Harrowfield, *J. Am. Chem. Soc., 94,* 3425 (1972).
13 D. Yang and D. A. House, *Inorg. Chim. Acta, 74,* 179 (1983).
14 C. J. Hawkins, G. A. Lawrance and R. M. Peachey, *Aust. J. Chem., 30,* 2115 (1977).
15 D. A. House, *J. Inorg. Nucl. Chem., 35,* 3103 (1973).
16 I. J. Kindred and D. A. House, *J. Inorg. Nucl. Chem., 37,* 1359 (975).
17 E. V. McKee and D. A. House, unpublished results.
18 Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Jpn., 35,* 1131 (1962).
19 J. E. Hughey, 'Inorganic Chemistry', Harper and Row, New York, 1978, p. 301.