The Synthesis of *cis*-$CrCl(en)_2(DMSO)^{2+}$ and *s-fac*-$CrCl(dien)(DMSO)_2^{2+}$ Salts*

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Although a number of synthetic routes can be used in the preparation of Cr(III) polyamine complexes [1, 2], the use of $CrCl_3 \cdot 6H_2O$ dehydrated in dipolar aprotic solvents (DMF or DMSO) has proved popular in recent years. The two solvents often yield different products on reaction with the same polyamine and Cr–Cl bond formation is favoured in DMF. Thus, while *cis*-$[CrCl_2(en)_2]Cl$ and *mer*-$CrCl_3$(dien) crystallise from the hot solution when en or dien are added to $CrCl_3 \cdot 6H_2O$ dehydrated in boiling DMF, the solution remains homogenous under the same conditions when DMSO is used.

In this letter we report the isolation of salts of *cis*-$CrCl(en)_2(DMSO)^{2+}$ and *s-fac*-$CrCl(dien)(DMSO)_2^{2+}$ which appear to be the major 2+ charged products formed in DMSO. A small scale, multi-step synthesis of *cis*-$[CrCl(en)_2(DMSO)]ClO_4 \cdot NO_3$ has previously been described [3].

Experimental

Caution: although we have experienced no difficulties with the perchlorate salts described here, they should be regarded as potentially explosive and handled accordingly. Working with boiling DMSO requires a very efficient fume hood if odour complaints are to be avoided.

cis-Chloro(diethylenetriamine)bis(dimethylsulfoxide)-chromium(III) Salts

A magnetically stirred solution of hydrated chromium(III) chloride (50 g, reagent grade) was boiled (190 °C) in DMSO (200 ml) for 1–1½ h, until the volume was reduced to about 175 ml. Diethylenetriamine (20 ml, Fluka, technical grade) was added when the now purple coloured solution had cooled to about 100 °C. The heat of reaction caused the temperature to rise to almost boiling and the resulting dark green coloured solution was maintained at about 120 °C for 30 min before cooling to about 50 °C. The still warm DMSO solution was then poured into a solution of 6 M HCL (400 ml) containing 50 g of $ZnCl_2$. Ice cooling resulted in the slow deposition of the crude $ZnCl_4^{3-}$ salt (purple crystals, 40 g, 38%) which were collected by filtration and washed successively with 2-propanol and ether and air dried.

The crude product was recrystallised as the $ZnCl_4^{2-}$ or ClO_4^- salts in 20 g batches. The solid was placed on a coarse (pore #2) sintered glass filter funnel (7 cm diam.) and extracted by gentle suction with 5–7 × 25 ml portions of 0.1 M HCl at room temperature into an ice cooled flask containing solid $NaClO_4$ (20 g) for the perchlorate salt or $ZnCl_2$ (20 g) dissolved in 3 M HCl (50 ml) for the $ZnCl_4^{2-}$ salt.

After 15 min ice cooling the deposited products [violet crystals, 9 g ClO_4^- salt (47%) or 12 g $ZnCl_4^{2-}$ salt (60%)] were collected by filtration and washed and dried as above. *Anal.* Calc. for $[CrCl(dien)(DMSO)_2](ClO_4)_2$, $CrC_8H_{25}N_3Cl_3S_2O_{10}$: C, 17.60; H, 4.62; N, 7.70. Found: C, 17.55; H, 4.79; N, 7.71%. Calc. for $[CrCl(dien)(DMSO)_2]ZnCl_4$, $CrC_8H_{25}N_3S_2O_2ZnCl_5$: C, 17.34; H, 4.55; N, 7.59. Found: C, 16.91; H, 4.81; N, 7.51%. Visible absorption spectra** (H_2O); ClO_4^- salt: λ_{max} 549 (94.1), λ_{min} 460 (14.8), λ_{max} 398 (51.5); $ZnCl_4^{2-}$ salt: λ_{max} 550 (93.9), λ_{min} 460 (13.9), λ_{max} 398 nm (49.1 M^{-1} cm^{-1}. Perchlorate salt in DMSO, λ_{max} 550 (104), λ_{min} 461 (15.9), λ_{max} 398 (54.4).

cis-Chloro(dimethylsulfoxide)bis(ethylenediamine) chromium(III) Salts

The crude tetrachlorozincate salt (red crystals, 96 g, 52%) was prepared in essentially the same manner as the dien analogue, except that 100 g of $CrCl_3 \cdot 6H_2O$ dehydrated in 200 ml of DMSO were reacted with 45 ml of anhydrous en, and the product crystallised from 400 ml of 6 M HCl containing 100 g of $ZnCl_2$.

This cation is rather more stable to solvolysis than the dien analogue and can be recrystallised in good yield from water as the pure $ZnCl_4^{2-}$ or $ClO_4^- \cdot NO_3^-$ salts [3] using conventional techniques.

Thus 20 g of the crude $ZnCl_4^{2-}$ salt dissolved in 200 ml of H_2O at 40 °C followed by 20 g each of $NaClO_4$ and $NaNO_3$ and ice cooling gave 14 g (78%) of the pure $ClO_4^- \cdot NO_3^-$salt. The pure $ZnCl_4^{2-}$ salt (16 g, 80%) was isolated in a similar manner by addition of 30 g of $ZnCl_2$ dissolved in 100 ml of 6 M HCl. In all cases the products were washed and dried as for the dien analogues. *Anal.* Calc. for $[CrCl(en)_2(DMSO)]ZnCl_4$, $CrC_6H_{22}N_4SOZnCl_5$: C, 14.62; H, 4.50; N, 17.35. Found: C, 14.48; H, 4.74;

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*Abbreviations used: en = 1,2-diaminoethane = ethylenediamine; dien = diethylenetriamine = $NH_2(CH_2)_2NH(CH_2)_2NH_2$; DMF = dimethyl formamide; DMSO = dimethyl sulfoxide; *N*-Me-tn = $CH_3NH(CH_2)_3NH_2$.

**Mean of three determinations.

N, 11.51%. Calc. for $[CrCl(en)_2(DMSO)]ClO_4 \cdot NO_3$, $CrC_6H_{22}N_5Cl_2SO_8$: C, 16.11; H, 4.96; N, 15.66. Found: C, 15.84, H, 5.11, N, 15.59%. Visible absorption spectra* (H_2O) $ZnCl_4^{2-}$ salt: λ_{max} 514 (75.4), λ_{min} 445 (18.5), λ_{max} 391 (55.5); $ClO_4^- \cdot NO_3^-$ salt: λ_{max} 514 (75.2), λ_{min} 445 (18.4), λ_{max} 392 nm (55.2 M^{-1} cm^{-1}). *cf.* *cis*-$CrCl(en)_2(OH_2)^{2+}$ (0.1 M HCl) [4] λ_{max} 512 (73.5), λ_{min} 440 (21.9), λ_{max} 387 (60.0). Perchlorate·nitrate salt in DMSO: λ_{max} 517 (87.7), λ_{min} 447 (22.7), λ_{max} 394 (68.4). Literature [3]; $ClO_4^- \cdot NO_3^-$ salt (DMSO); 532 (84.4); 550 (67.2); 586 nm (26.0 M^{-1} cm^{-1}).

Results and Discussion

The $ZnCl_4^{2-}$ salts of $CrCl(en)_2(DMSO)^{2+}$ and $CrCl(dien)(DMSO)_2^{2+}$ are easily synthesised on the ~50 g scale from readily available starting materials. These salts are reasonably soluble in water, but almost insoluble in HCl > 3 M and DMF or DMSO. The corresponding perchlorate or mixed nitrate perchlorate respectively are obtained by metathesis and are soluble in water, 0.1 M HCl, DMF and DMSO.

Visible absorption spectral parameters are normal for this type of Cr(III) complex and the data for *cis*-$CrCl(en)_2(H_2O)^{2+}$ [4] and *cis*-$CrCl(en)_2(DMSO)^{2+}$ are very similar. Interestingly, the extinction coefficients are approximately 9% greater in DMSO than in water, but the wavelengths at the maxima or minima are unchanged.

The geometric configuration of the bis(ethylenediamine) cation is almost certainly *cis*, as evidenced by the symmetrical absorption spectra and the equivalence of the extinction coefficients with these established previously for *cis*-$CrCl(en)_2(DMSO)^{2+}$ [3]. The configuration of the dien complex is more speculative. The triamine ligand is probably in the *fac* arrangement as the complex can be anated with Cl^- to give green *fac*-$CrCl_3$(dien) [5] We propose the *s-fac* configuration for the monodentate ligands with the chloro ligand *trans* to the *sec*-NH group of the triamine, as $CrCl(dien)(DMSO)_2^{2+}$ generally** reacts with diamines to produce *s-fac*-$CrCl(dien)(diamine)^{2+}$ [6].

The *cis*-$CrCl(en)_2(DMSO)^{2+}$ and *s-fac*-$CrCl(dien)(DMSO)_2^{2+}$ cations are reasonably inert in dilute aqueous acidic solution at room temperature, but at 50 °C measurable hydrolysis occurs. Spectrophotometric measurements with time at 50 °C (0.1 M $HClO_4$) suggests that chloride release is taking place, but we cannot exclude concurrent or subsequent DMSO solvolysis as well. Both complexes generate good isosbestic points during the hydrolysis reaction [381, 434, 498 nm for *cis*-$CrCl(en)_2(DMSO)^{2+}$ and 380, 448, 523 nm for *s-fac*-$CrCl(dien)(DMSO)^{2+}$] and the final absorption spectra are similar to *cis*-$Cr(en)_2(OH_2)_2^{3+}$ [8] and *fac*-Cr(dien) $(OH_2)_3^{3+}$ [9]. However, with the present data, we would not expect to distinguish these from *cis*-$Cr(en)_2(OH_2)(DMSO)^{3+}$ or *fac*-$Cr(dien)(OH_2)(DMSO)_2^{3+}$

Spectrophotometrically determined half-lives for the hydrolysis of *cis*-$[CrCl(en)_2(DMSO)]ClO_4 \cdot NO_3$ and *s-fac*-$[(CrCl(dien)(DMSO)_2](ClO_4)_2$ in 0 1 M $HClO_4$ at 50 °C are 38 ± 1 and 12 ± 0.5 min, respectively.

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References

1 C. S. Garner and D A. House, *Transition Met. Chem.*, *6*, 59 (1970).

2 J. C Chang, *J. Ind. Chem. Soc*, *LIV*, 98 (1977).

3 D. A. Palmer and D A. Watts, *Aust J Chem.*, *21*, 2895 (1968).

4 D. A. House and C S. Garner, *J Inorg Nucl. Chem*, *28*, 904 (1966)

5 A D. Fowlie, D. A. House, W T. Robinson and S Sheat-Rumbal, *J Chem Soc. A*, 803 (1970)

6 D. A. House, *Inorg Nucl. Chem. Lett*, *12*, 259 (1976), B. S. Dawson and D A. House, *Inorg Chem*, *16*, 1354 (1977).

7 D. A. House, *Inorg Chim. Acta*, submitted for publication

8 F. Woldbye, *Acta Chem Scand*, *12*, 1079 (1958).

9 S H. Caldwell and D A. House, *J. Inorg Nucl. Chem.*, *31*, 811 (1969).

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*Mean of three determinations.

**We have recently found a $CrCl(dien)(diamine)^{2+}$ system where the polyamine arrangement is *u-fac* (diamine = *N*-Me-tn) [7].