TABLE I.

Complex	M.p.	colour	μ(eff.)	νRe=O	νC=N	νC–O	νRe–X
$ReCl_2(Me\text{-}sal)(PMe_2Ph)_2$	183	red	2.1		1589	1297	308
$ReBr_2(Me\text{-}sal)(PMe_2Ph)_2$	204	red	2.0		1590	1289	
$ReCl_2(Ph\text{-}sal)(PMe_2Ph)_2$	207	red	2.1		1590	1288	310
$ReBr_2(Ph\text{-}sal)(PMe_2Ph)_2$	190	red	2.0		1588	1286	
$Re_2Cl_4(sal_2en)(PMe_2Ph)_4$	199	red	2.0		1605	1300	308
cis-$ReOCl_2(Me\text{-}sal)PMe_2Ph$	182	light green	diam.	965	1610	1285	320, 292
trans-$ReOCl_2(Me\text{-}sal)PMe_2Ph$	179	dark green	diam.	975	1609	1290	308
cis-$ReOCl_2(Ph\text{-}sal)PMe_2Ph$	229	bright green	diam.	976	1600	1290	318, 273
cis-$ReOCl_2(oxine)PMe_2Ph$	274	dark green	diam.	962		1316	329, 290
trans-$ReOCl_2(oxine)PMe_2Ph$	258	dark green	diam.	974		1319	300
$Re_2O_2Cl_4(sal_2en)(PMe_2Ph)_2$	241	emerald green	diam.	960	1600	1285	321

the *trans*-$ReX_2(S.B.)(PMe_2Ph)_2$ complexes were obtained (save when S.B. = Oxine), with a reduction of rhenium from (V) to (III). The reaction goes through the formation of *cis* or *trans*-$ReOX_2(S.B.)PMe_2Ph$, according to the starting isomer, where the substitution of PPh_3 with PMe_2Ph is observed.

$$ReOX_2(S.B.)PPh_3 \xrightarrow[(PhH)]{PMe_2Ph}$$

$$ReOX_2(S.B.)PMe_2Ph \xrightarrow[(PhH)]{PMe_2Ph}$$

$$ReX_2(S.B.)(PMe_2Ph)_2$$

The intermediate complexes were isolated only when the *cis* and *trans*-$ReOCl_2(Me\text{-}sal)PPh_3$, *cis*-$ReOCl/(Ph\text{-}sal)/PPh_3$, *trans*-$Re_2O_2Cl_4/(sal_2en)/(PPh_3)$ and *cis* and *trans*-$ReOX_2(oxine)PPh_3$ starting complexes were used. The *cis* isomers, with the exception of the complexes with Oxine ligand, were collected only when the reaction was carried out at room temperature. We can notice that the substitution of PPh_3 keeps the conformation unchanged. When 8-hydroxyquinolinate complexes are used only the substitution occurs and the reduction of rhenium involves the leaving of this ligand and the formation of the known $ReX_3(PMe_2Ph)_3$ complexes.

The reduction occurs with all the other complexes, even though the reaction time is very different according to the compound symmetry and, with subordinate importance, to the used Schiff base. *Cis* derivatives in general react very easily in respect to *trans* analogues as well as Ph-sal complexes in respect to the sal_2en or Me-sal analogues. It is important to notice that both *cis* and *trans* rhenium(V) complexes give rise to reduced complexes with the same *trans* configuration.

The characterization of all the complexes was performed by elemental analysis, magnetic susceptibility measurements in solid and in solution, i.r. spectra. In Table I some general properties and important i.r. frequencies are reported.

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Solvent Dependent Stereochemistry of Cyanide Anation of Some Chromium(III) Complexes

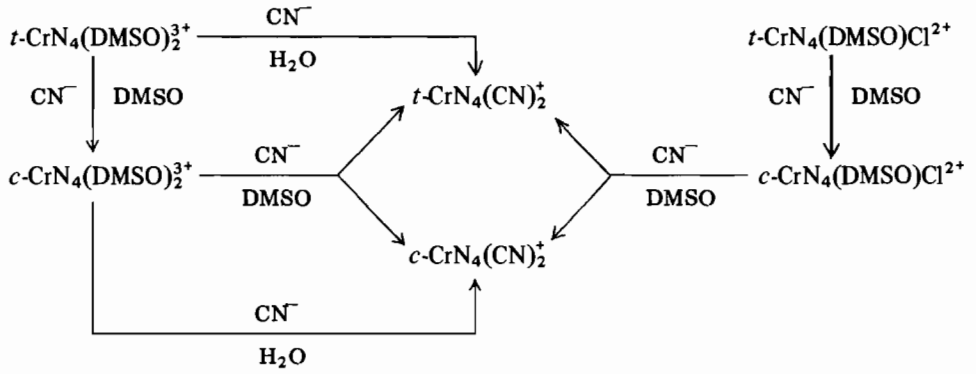
PIETRO RICCIERI and EDOARDO ZINATO

Dipartimento di Chimica, Università di Perugia, 06100 Perugia, Italy

The usual synthetic route to acidoamminechromium(III) ions is replacement of H_2O ligands by anionic groups [1]. So far, cyanoammine complexes have not been reported; a possible reason is that cyanide cannot be bound to chromium by such a procedure, as deprotonation of coordinated water by this strongly basic anion prevents substitution in both aqueous and nonaqueous media. An alternative reaction was therefore sought to obtain the previously unknown *trans*- and *cis*-$Cr(NH_3)_4(CN)_2^+$ species, particularly in order to investigate their

excited-state reactions. The photochemical interest arises from the extreme spectrochemical position and the π-acceptor bonding of the CN^- ligand. The method is one of CN^- anation of $Cr(NH_3)_4(DMSO)_2^{3+}$ compounds (DMSO = dimethylsulfoxide), and this report concerns the role of the solvent in determining the stereochemistry of the products.

Due to the absence of acidic hydrogens, substitution of DMSO takes place smoothly either in water or in DMSO as solvent. The general pattern of reactivity is summarized in the following Scheme (where N = NH_3):



The product yield is larger in the dipolar aprotic solvent than in water, because of various factors: (*a*) the enhancement of ion association [2]; (*b*) a poorer anion solvation [3]; (*c*) the absence of any hydrolysis.

Reaction of either *trans*- or *cis*-$Cr(NH_3)_4(DMSO)_2^{3+}$ in DMSO leads to an identical mixture of *trans*- and *cis*-$Cr(NH_3)_4(CN)_2^+$ cations, as the presence of CN^- induces fast and complete *trans* → *cis* isomerization, prior to anation.

Stereomobility of chromium(III) species is possible in this solvent [4] and ion pairing with the entering anion may drive the equilibrium mixture towards the polar *cis* form. An unexpected finding is that partial *cis* → *trans* isomerization (the direction is rather uncommon for Cr(III)) accompanies successive entry of CN^-. In this stage, the decreased (1+) complex charge should disfavor ion pairing stabilization with respect to mutual repulsion of the coordinated CN^- groups. Exactly the same result is achieved starting from either *trans*- or *cis*-$Cr(NH_3)_4(DMSO)Cl^{2+}$.

Although less efficient, anation in H_2O occurs with retention of configuration, as is generally observed for chromium(III) substitutions in aqueous solution [1, 5]. In either case relatively fast subsequent coordination of more CN^- subtracts part of the product, to yield the neutral $Cr(NH_3)_3(CN)_3$ species.

TABLE I. Ligand-Field Absorption Maxima of the $Cr(NH_3)_4(CN)_2^+$ Ions in Water.

Transition	*trans* Isomer λ, nm (ε)		*Cis* isomer λ, nm (ε)	
$^4B_1 \rightarrow {}^4B_2, {}^4E\ (^4T_{2g})$	440	(42.6)	436	(49.0)
$^4B_1 \rightarrow {}^4E, {}^4A_2\ (^4T_{1g})$	344	(41.5)	342	(37.2)

Both dicyanotetraammine complexes were isolated and characterized by elemental analysis. Their 1+ charge was confirmed by electrical conductance and ion-exchange tests. The IR spectrum exhibits the stretching frequency of coordinated cyanide at 2130 cm^{-1}. The ligand-field absorption maxima, reported in Table I, agree with theoretical predictions [6]. Even though the electronic spectra of the individual isomers are not sufficiently diagnostic of the configurations, definite stereochemical evidence is provided by the respective products of acid hydrolysis, *trans- and cis*-$Cr(NH_3)_4(H_2O)_2^{3+}$, which are formed with complete stereoretention and present significantly different absorption features.

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