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Reactions of the Pentahalogenonitrosylrhenate Anions $[Re(NO)X_5]^{2-}$ (X = Cl, Br) with Solvents

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We are currently studying the reactivity of the pentahalogenonitrosylrhenate $[Re(NO)X_5]^{2-}$ [1,2] with several neutral ligands such as phosphines, phosphites, carbon monoxide, amines and solvents able to act as donors. This letter describes the compounds we have obtained by reaction with solvents (methanol, ethanol, n-propanol, n-butanol, acetonitrile, dimethylsulphoxide) of the chloro and bromo compounds.

Nearly 0.2 g of $[Re(NO)X_5](NEt_4)_2$ (X = Cl, Br) are refluxed in 50 ml of the proper solvent for 3 hr. The hot suspension is filtered and then cooled and concentrated to 20 ml. Green crystalline compounds, $[Re(NO)X_4L]NEt_4$ (L = solvent molecule), are obtained and are listed in Table I (I - X).

The green compounds $[Re(NO)Cl_5](NEt_4)_2$ and $[Re(NO)Br_5](NEt_4)_2$, insoluble in non-polar solvents, dissolve in solvents such as alcohols, acetonitrile and dimethylsulphoxide and react under reflux giving the species $[Re(NO)X_4L]^-$. Usually the reactions are carried out very easily and in a short time. These compounds (I - X) are indefinitely stable paramagnetic species. The values of their molar conductivities are in good agreement with those predicted for 1:1 electrolytes. The IR spectra exhibit a strong band in the region 1750 - 1735 cm^{-1}, assigned to the stretching mode of the nitrosyl group. Other important IR bands are due to the vibrational modes of the bonded solvent molecules, the frequency values being similar to the values observed in the free substances.

$[Re(NO)Cl_5]^{2-}$ is less reactive than the bromo analogue. In the former case it was impossible to obtain the derivatives with n-propanol and n-butanol; upon heating, the solution turns to a brown color indicating the formation of decomposition products.

The ability of $[Re(NO)X_5]^{2-}$ to undergo substitution of a X^- ligand by a solvent molecule indicates the higher reactivity of one of the five halogen atoms. This may be due to a *trans* effect of the nitrosyl group, so that the solvent molecule should occupy the position *trans* to this ligand. X-Ray single crystal analyses performed on $[Re(NO)Br_4(MeCN)]NEt_4$ and $[Re(NO)Br_4(EtOH)]NEt_4$ have confirmed this prevision, showing moreover that the NO ligand is linearly coordinated to the metal.[3]

The replacement of an halide ion by a solvent molecule is reversible. Upon treatment of the solvent derivatives with concentrated halogenidric acid solutions the parent pentahalide compounds can be re-obtained. Moreover, it is possible to substitute a bonded solvent with a different species by dissolution of $[Re(NO)X_4L]^-$ in the suitable solvent and refluxing.

TABLE I. Analytical and Chemico-physical Data.

Compound		Λ_m[a]	μ_{eff}[b] (B.M.)	ν_{NO}[c]	C		H		N		O	
					Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
I	$[Re(NO)Cl_4(MeOH)]NEt_4$	29.7	1.75	1750	20.7	20.1	4.61	4.35	5.35	5.33	6.15	6.10
II	$[Re(NO)Cl_4(EtOH)]NEt_4$	31.3	1.78	1745	22.4	21.9	4.86	4.62	5.24	5.13	5.99	5.79
III	$[Re(NO)Cl_4(MeCN)]NEt_4$	32.9	1.70	1740	22.7	22.9	4.34	4.21	7.93	7.61	–	–
IV	$[Re(NO)Cl_4(DMSO)]NEt_4$[d]	29.8	1.79	1740	21.2	21.5	4.59	4.38	4.94	5.06	–	–
V	$[Re(NO)Br_4(MeOH)]NEt_4$	34.6	1.78	1750	15.5	15.6	3.43	3.34	4.01	3.84	4.59	4.43
VI	$[Re(NO)Br_4(EtOH)]NEt_4$	29.5	1.75	1747	16.8	17.0	3.65	3.66	3.93	3.86	4.49	4.86
VII	$[Re(NO)Br_4(n\text{-}PrOH)]NEt_4$	31.4	1.77	1740	18.2	18.5	3.85	4.10	3.87	3.57	4.40	4.65
VIII	$[Re(NO)Br_4(n\text{-}ButOH)]NEt_4$	30.1	1.76	1740	19.4	19.3	4.05	3.95	3.78	3.95	4.32	4.20
IX	$[Re(NO)Br_4(MeCN)]NEt_4$	35.5	1.73	1735	16.9	16.7	3.25	3.10	5.96	5.82	2.16	1.98
X	$[Re(NO)Br_4(DMSO)]NEt_4$	29.8	1.76	1740	16.1	16.5	3.49	3.30	3.76	3.75	4.30	4.13
XI	$[Re(NO)Cl_4]NEt_4$	–	1.75	1755	19.6	19.7	4.08	4.20	5.72	5.64	3.38	3.51
XII	$[Re(NO)Br_4]NEt_4$	–	1.72	1748	14.4	14.8	3.00	3.06	4.22	4.22	2.42	2.72

[a] In nitrobenzene solution. [b] Gouy balance method. [c] In nujol mull. [d] DMSO = dimethylsulphoxide.

Upon heating, the green crystals of these compounds turn to brown, losing solvent. The derivatives containing alcohols and acetonitrile undergo this displacement between 120 °C and 140 °C; beyond these temperatures all the chloro complexes (as well as all the bromo complexes) behave as a single compound melting at 195 °C (at 187 °C, respectively). By this way we have obtained the compounds XI and XII of Table I. These five-coordinate brown species dissolve in warm alcohols, acetonitrile and cold dimethylsulphoxide giving solutions from which the green compounds containing solvents can be re-obtained.

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References

1 D. Giusto and G. Cova, *Gazzetta, 102,* 265 (1972).

2 J. A. Casey and R. K. Murmann, *J. Am. Chem. Soc., 92,* 78 (1970).

3 G. Ciani, D. Giusto, M. Manassero and M. Sansoni, *J. Chem. Soc. Dalton,* in the press.