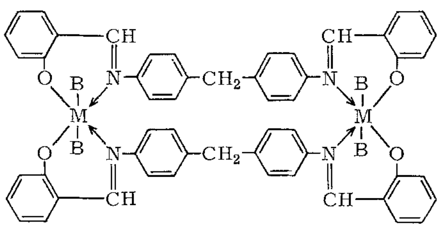
Table 1. Analyses, conductance, magnetic susceptibility and i.r. spectral data for the Schiff base complexes.

Compound	Found (Calcd.)% Metal	N	Mol. wt. Found (Calcd.)	μ_{eff} (B.M.)	ν(C=H) ν(C–O)	ν(M–N) ν(M–O)
LH_2	–	6.6 (6.9)		–	1615 1490	–
$[Co_2L_2(H_2O)_4]$	11.7 (11.8)	5.5 (5.6)	985 (998)	2.58	1605 1445	510 450
$[Cu_2L_2(H_2O)_4]$	12.5 (12.6)	5.5 (5.5)	998 (1007)	1.20	1600 1450	510 445
$[Ni_2L_2(H_2O)_4]$	11.6 (11.7)	5.5 (5.6)	989 (997)	2.32	1600 1460	505 460
$[Zn_2L_2(H_2O)_4]$	12.7 (12.9)	5.4 (5.5)	1004 (1010)	–	1605 1455	510 440
$[Cd_2L_2]$	13.3 (13.4)	5.9 (6.0)	1095 (1104)	–	1600 1460	505 450
$[Hg_2L_2]$	32.9 (33.2)	4.5 (4.6)	1275 (1281)	–	1605 1450	510 455

sub-normal magnetic moments, spectra, high melting points and insolubility in common organic solvents, the cobalt(II), copper(II) and nickel(II) complexes presumably possess a dinuclear structure. The zinc(II) complex may be dinuclear octahedral and the cadmium(II) and mercury(II) complexes presume to possess a dimeric tetrahedral configuration.

The complexes can be represented by the following structure.



$M = Co^{II}, Cu^{II}, Ni^{II}$ or Zn^{II}; $B = H_2O$
$M = Cd^{II}$ or Hg^{II}; B absent

References

(1) R. H. Holm and G. W. Everest (Jr), *J. Am. Chem. Soc., 88,* 2442 (1966). – (2) J. C. Bailar and H. A. God winard, *J. Am. Chem. Soc., 63,* 2467 (1961). – (3) D. G. Hodgson, *Prog. Inorg. Chem., 19,* 173 (1975). – (4) R. Whyman and E. Hatfield, *Transition Met. Chem., 5,* 47 (1969). – (5) B. Sahoo and J. Chakravarty, *Ind. J. Chem., 20A,* 431 (1981). – (6) B. B. Mahapatra and S. K. Pujari, *Chemical Tech. and Biotech.* (UK), in press. – (7) B. B. Mahapatra, D. Panda and B. K. Patel, *Acta Chim. (Hung),* in press. – (8) B. B. Mahapatra and S. K. Pujari, *Acta Chim. (Hung),* in press. – (9) J. E. Covacis, *Spectrochim. Acta, 23A,* 183 (1967). – (10) P. Teyssi and J. J. Charrettee, *Spectrochim. Acta, 19,* 1407 (1965).

(11) K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds,* Wiley, New York, 1963. – (12) I. Gamo, *Bull. Chem. Soc., 34,* 760 (1961). – (13) J. R. Ferraro, *Low Frequency Vibrations of Inorganic and Coordination Compounds,* Plenum Press, New York, 1971. – (14) A. B. P. Lever, *Inorganic Electronic Spectroscopy,* Elsevier, Amsterdam, 1968. – (15) C. J. Ballhausen, *Introduction to Ligand Field Theory,* McGraw Hill, New York, p. 268 1962.

(Received January 3rd, 1984) TMC 1088

A Very Simple Synthesis of $K_3[Re(NO)(CN)_5] \cdot 2\,H_2O$ Directly from $[ReO_4]^-$: Existence of Two Structural Isomers in Aqueous Medium as Indicated by ^{13}C N.m.r. Spectroscopy

Ramgopal Bhattacharyya* and Partha S. Roy

Department of Chemistry, Jadavpur University, Calcutta 700032, India.

Summary

Perrhenate(VII) was reductively nitrosylated using an excess of CN^-, OH^- and $NH_2OH \cdot HCl$, and from the reaction mixture $K_3[Re(NO)(CN)_5] \cdot 2H_2O$ has been isolated. Its aqueous solution behaves as a 3:1 electrolyte and its ^{13}C n.m.r. spectrum in D_2O solution suggests that the complex molecule forms two types of isomeric structure arising from the two different modes of intramolecular hydrogen (deuterium) bonding of the two lattice water (D_2O in the bulk solvent) molecules.

Introduction

Among the cyanonitrosyl complexes of various transition metal ions(1), the rhenium derivatives are most controversial(2–4). The first such compound was reported by Wilkinson and co-workers(5), who formulated it as $Ag_3[Re(NO)(CN)_7]$ (though the possibility of its formulation as $Ag_3[Re(NO)(CN)_5]$(5, 6) could not be eliminated in the absence of detailed analytical and physico-chemical data). It was obtained by treating $[Re(CN)_8]^{3-}$ (the existence of which, however, could not be confirmed by Griffith *et al.*(7)) with HNO_3. Later, an extremely brief report(8) was made on the existence of the complex, $[Re(NO)(CN)_5]^{2-}$, prepared by treating

---

* Author to whom all correspondence should be directed.

0340–4285/84/0707–0281$02.50/0

$[Re(CN)_5H_2O]^{3-}$ with HNO_3. In this case also, several authors(3, 4) expressed doubts regarding the authenticity of the nitrosyl compound. Recently, Sergeeva *et al.*(9) reported the compound $K_3[Re(NO)(CN)_7] \cdot 4\,H_2O$, obtained by the reductive nitrosylation of $KReO_4$ using $NH_2OH \cdot HCl$ and KCN in an aqueous alkaline medium. Griffith *et al.*(7) have reinvestigated the above work and claimed that the composition of the complex obtained by Sergeeva *et al.* is $K_3[Re(NO)(CN)_5] \cdot 3\,H_2O$. However, both the above reports(7, 9) warrant further investigation due to the complete lack of experimental details and insufficient physico-chemical data to support the proposed formulations.

We have recently shown(10) that $[ReO_4]^-$ undergoes a facile conversion to generate the $\{Re(NO)\}^{2+}$ moiety with an excess of $NH_2OH \cdot HCl$ as the nitrosylating agent in the presence of SCN^- or N_3^-, in aqueous alkali. It was considered worthwhile to investigate whether the above conversion also takes place in the presence of CN^-. The basic motive behind this work is, however, to synthesize and characterise thoroughly a cyanonitrosyl complex of rhenium, over the existence and exact formulation of which there have been considerable differences of opinion.

Experimental

Materials and methods

The ^{13}C n.m.r. spectrum was recorded using a Bruker WB 500 NMR (500 MHz) spectrometer against the sodium salt of trimethylsilyl propionate (TSP) as an internal standard. For other details see ref. 11.

Preparation of $K_3[Re(NO)(CN)_5] \cdot 2\,H_2O$

A mixture of $K[ReO_4]$ (1.0 g, 3.5 mmol), KCN (2.3 g, 35 mmol) and KOH (5.9 g, 105 mmol) was dissolved in a minimum volume of hot water (*ca.* 90 °C). To this hot solution, solid $NH_2OH \cdot HCl$ (3.65 g, 52.5 mmol) was added portionwise with stirring. The hot solution was stirred for another 15 min to drive out the NH_3 evolved. A deep crimson solution was obtained. The solution was then cooled to 0 °C and the ice-cold solution was subsequently poured slowly into chilled dry *i*-PrOH (100 cm^3) and stirred magnetically for 10–15 min keeping the temperature of the solution mixture below 5 °C. A deep crimson-lake coloured oil was separated out. The colourless supernatant liquid was carefully decanted off and the oil was again poured into fresh cold *i*-PrOH (100 cm^3) and the mixture was shaken until the oil thickened. This process was repeated 3–4 times using fresh *i*-PrOH in each operation. Then a chilled *i*-PrOH–MeOH mixture (3 : 1) was added dropwise to the oil with occasional stirring until the oil solidified. The alcohol mixture was decanted off and the dark red solid so obtained was washed thoroughly with *i*-PrOH and then dried over $CaCl_2$ under reduced pressure. The crude product was extracted with dry MeOH. Addition of n-C_6H_{14}/Et_2O (1 : 1) mixture to the cold MeOH extract resulted in a separation of a burnt-amber microcrystalline solid which was filtered off, washed with *i*-PrOH and pentane and vacuum dried. Yield: 0.6 g, 35%. (Found: C, 11.8; H, 0.7; N, 16.5; K, 24.3 and H_2O, 7.0. $K_3[Re(NO)(CN)_5] \cdot 2H_2O$ calcd. C, 12.0; H, 0.8; N, 16.8; K, 23.4 and H_2O, 7.2%.) The compound is hygroscopic.

Results and Discussion

The conversion of $[ReO_4]^-$ to $[Re(NO)(CN)_5]^{3-}$, the synthetic process described here, has a single step and requires only a single pot, although isolation of a pure substance requires additional steps. Both Sergeeva *et al.*(9) and Griffith *et al.*(7) mentioned that the potassium salt of the cyanonitrosyl complex isolated by them is orange-red and is soluble only in water. However, our product is burnt-amber, and, apart from its water solubility it is also soluble even in anhydrous methanol and the aqueous solution of the complex behaves as a 3 : 1 electrolyte(12). Moreover, Griffith *et al.*(7) isolated the tetraphenylphosphonium and arsonium salts of the anion although they did not report any experimental procedure. Our experience is that the isolation of those salts *via* cation metathesis is impossible.

The i.r. vibrational frequencies of the compounds as reported in the literature as well as the corresponding data of our product are compared in the Table. The assignment to ν(NO) obtained in the present work agrees with that made by

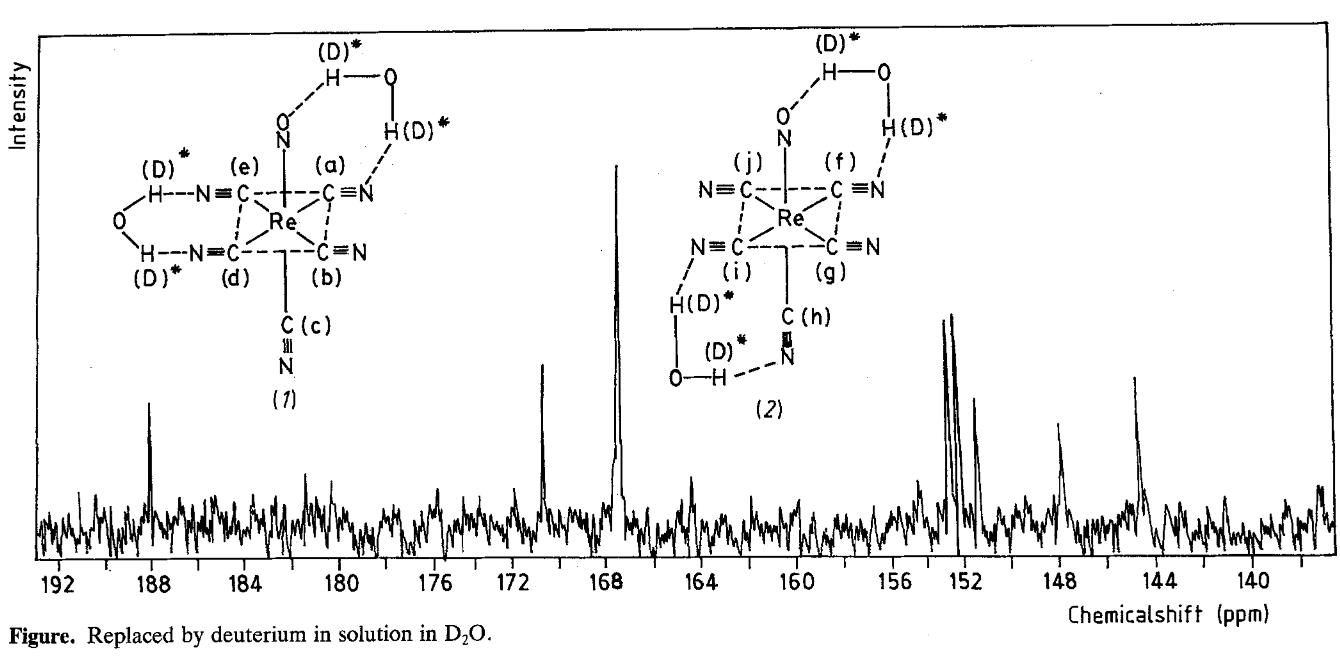


Figure. Replaced by deuterium in solution in D_2O.

Table 1. I.r. and electronic spectral data of the cyanonitrosyl complexes.

Compound	I.r. vibrational frequencies (cm^{-1})a) ν(CN)		ν(NO)	ν_{ReN}(NO)	ν(ReC)	δ(ReNO)	δ(ReCN)	Electronic absorptions (nm)b)
$K_3[Re(NO)(CN)_5] \cdot 2H_2O$ (present work)	2170(m) 2075(s)	2120(w) 2050(sh)	1650(s)	620(sh)	450(w)	495(w)	360(w)	480(75) 375(10) 285(350)
$K_3[Re(NO)(CN)_5] \cdot 3H_2O$ (compound of Griffith *et al.*)	2141(m) 2080(s)	2110(m) 2045(s)	1650(s)	592(w)c)	445(s)c)	480(s)c)	d)	e)
$K_3[Re(NO)(CN)_7] \cdot 4H_2O$ (compound of Sergeeva *et al.*)	2090	2110	1730	518f)	405f)	622f)	445f)	e)

a) For the assignments of the i.r. bands, see Refs. 6 and 13; b) In aqueous solvent, the molar absorptivities are shown in parenthesis; for assignments see text; c) Not originally assigned; the assignments are made on the basis of the data reported by the authors; d) The remaining bands are: 425(m), 398(m), 375(m), 362(w) and 310(w); e) Not reported; f) Assignment of these bands by the authors (refs. 6 and 13) does not conform with ours.

Griffith *et al.*, whereas Sergeeva *et al.* assigned a band at a higher frequency. Also, with one exception the assignments to ν(CN) compare with those of Griffith *et al.*, although they observed a greater number of bands in the lower wave number region (Table).

The endothermic elimination (DTA and TGA) of the two lattice water molecules at a relatively high temperature (*ca.* 110 °C) and also the broad half-width of the ν(NO) i.r. band suggest that the water molecules may be engaged in strong intramolecular hydrogen-bonding involving the NO group. This is also substantiated by the $^{13}C\{^1H\}$ n.m.r. spectrum of the compound in D_2O solution.

The molecule shows eight ^{13}C signals at 188.1, 170.8, 167.5, 152.5, 152.1, 151.4, 147.8 and 144.8 ppm with the respective relative areas roughly in the ratio 1:1:3:1:1:1:1:1 (Figure). These are assigned to cyanide carbons. This n.m.r. spectrum can be explained if it is assumed that the complex molecule forms two isomeric structures arising from two different modes of hydrogen bonding of the water molecules simultaneously with the NO and one or other of the CN groups as shown in the structures *(1)* and *(2)* in the Figure. Since both the structures have C_s symmetry, all the CN groups are non-equivalent and hence, ten signals of identical relative area should have been expected. The presence of eight signals of the stated intensities can account for ten CN groups in the two isomers; the apparent differences in the relative areas in some of the signals (Figure) may be due to the existence of different ammounts of the two isomers in D_2O. The three equatorial CN groups b, g, j in the Figure which are not involved in hydrogen-bonding accidently produce the degenerate signal at 167.5 ppm. The axial cyanide (c) in isomer *(1)*, which is not involved in hydrogen-bonding produces the signal at 144.5 ppm since back-bonding from metal to carbon is expected to be minimal here(10) [compare, for $[(CO)_2(Cp)Fe(CN)]$ $\delta(CN) = 154.7$ ppm whereas for $[(CO)(Cp)Fe(CN)_2]^-$ $\delta(CN)_{average} = 159.0$ ppm; see ref. (14)]). The remaining six signals are due to the six cyanides groups (a, d, e, f, h, i) involved in hydrogen-bonding in both isomers.

The absence of any signal at 169 ppm shows that the compound is free from any CN^- impurity(14), which is always an obstacle to the isolation of pure cyanonitrosyl complexes(4, 5). No Re–^{13}C coupling was observed in any of the eight ^{13}C signals, even at high resolution. The rhenium nuclei have spin values of 5/2(15). Also ^{15}N–^{13}C coupling was not observed. It may, however, be pointed out here that in the bulk D_2O solvent the two H_2O molecules are exchanged almost instantaneously which is obvious from the p.m.r. spectrum of the complex which was taken immediately after it was dissolved in D_2O. Also, the ^{13}C n.m.r. spectrum of the compound taken in a freshly prepared D_2O solution is identical with the spectrum taken 6 h after dissolution. So, it may be concluded that the labelling of the C-atoms (Figure) with respect to their mode or hydrogen-bonding in the solid remains valid in solution since deuterium-bonding is as strong(16) or even stronger(17) than the hydrogen-bonding. The title compound may be isostructural with the $K_3[V(NO)(CN)_5] \cdot 2H_2O$(18a) $[Co(C_{12}H_8N_2)_3]$-$[Cr(NO)(CN)_5] \cdot 2H_2O$(18b) and $K_3[Mn(NO)(CN)_5] \cdot 2H_2O$(18c), of known structure.

Considering the NO^+ formalism(19), the formal oxidation state of Re in this complex should be + I ($5d^6$), which is consistent with the diamagnetism of the complex. Although the molecule in both isomeric forms possesses C_s symmetry, the MO energy level diagram for C_{4v} symmetry may be valid(19) here on the basis of the local symmetry. In that case the three observed electronic absorption maxima (Table) may be assigned to $b_2 \rightarrow e$; $b_2 \rightarrow b_1$ and $b_2 \rightarrow a_1$ transitions.

Acknowledgements

Donation of the i.r. (PE 597) spectrophotometer used in this work by the Alexander von Humboldt Foundation is gratefully acknowledged. Sincere thanks are due to Dr. U. Banerjee (CALTECH, USA) and also to the Southern California Regional n.m.r. facility funded by Grant CHE-7916324 from NSF, USA, for recording the ^{13}C n.m.r. spectra. We also thank Dr. A. A. Bhattacharyya (Ohio State University, USA) for helpful discussions.

References

(1) K. G. Caulton, *Coord. Chem. Rev., 14,* 317 (1975). – (2) B. M. Chadwick and A. G. Sharpe, *Adv. Inorg. Chem. Radio Chem., 8,* 83 (1971). – (3) R. D. Peacock in J. C. Bailer (Ed.), *Comprehensive Inorganic Chemistry,* Vol. 3, Pergamon Press, N.Y., p. 905, 1975. – (4) A. G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals,* Academic Press, London, 1976. – (5) R. Colton, R. D. Peacock and G. Wilkinson, *J. Chem. Soc.,* 1374 (1960). – (6) W. P. Griffith, *Coord. Chem. Rev., 17,* 177 (1975). – (7) W. P. Griffith, P. M. Kiernan and J. M. Bregneelt, *J. Chem. Soc., Dalton Trans.,* 1411 (1978). –

(8) B. K. Sen and P. B. Sarkar, *Sci. Cult.*, *27*, 404 (1961); S. Sen, *Z. Anorg. Allgem. Chem.*, *335*, 222 (1965). – (9) A. Sergeeva, A. V. Mazera and A. Mazuroki, *Kood. Khim.*, *1*, 1681 (1975). – (10) R. G. Bhattacharyya and P. S. Roy, *Transition Met. Chem.*, *7*, 285 (1982); *Ibid.*, *J. Coord. Chem.*, *12*, 129 (1982); *Ibid*, *Indian J. Chem.*, *22A*, 111 (1983).

(11) R. G. Bhattacharyya, G. P. Bhattacharjee and A. M. Saha, *Transition Met. Chem.*, *8*, 255 (1983). – (12) S. Glasstone, *Textbook of Physical Chemistry*, Macmillan, London, 1972. – (13) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Interscience, N.Y., 1978. – (14) L. F. Farnell, R. W. Randall and E. Rosenberg, *Chem. Comm.*, 1078 (1971). – (15) B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radio Chem.*, *13*, 135 (1970). – (16) P. Schuster, G. Zundel and C. Sandorfy, *The Hydrogen Bond: Recent Developments in Theory and Experiments*, North-Holland Publ. Co., Oxford, p. 1229, 1976. – (17) P. Schuster, G. Zundel and C. Sandorfy, *J. Chem. Phys.*, *55*, 1373 (1971). – (18a) S. Jagner and N. G. Vennerberg, *Acta Chem. Scand.*, *32*, 3330 (1968); (b) P. T. Manoharan and H. L. Hamilton, *Inorg. Chem.*, *2*, 1043 (1963); (c) A. Tullberg and N. G. Vennerberg, *Acta. Chem. Scand.*, *21*, 1462 (1967). – (19) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, *13*, 339 (1974).

^{13}C n.m.r. spectrum and the probable isomeric structures of $K_3[Re(NO)(CN)_5] \cdot 2H_2O$ in D_2O solvent.

(Received September 7th, 1983;
in revised form February 28th, 1984) TMC 1036

Communication

Reactions and Molecular Structure of Di-μ-pentafluorothiolatobis-(1,5-cyclooctadiene)dirhodium(I)

Diana Cruz-Garritz, Bertha Rodríguez and Hugo Torrens*

D. E. Pg., Facultad de Química, Ciudad Universitaria, 04510 México D.F.

Javier Leal

Centro de Investigaciones en Química, U.A.N.L., Monterrey, Nuevo León, México

X-ray diffraction studies have shown that Rh_2Cl_2 skeleton in $[\{RhCl(COD)\}_2]$(1) (COD = 1,5-cyclooctadiene) is planar, whereas it is bent along the Cl–Cl axis in $[\{RhCl(CO)_2\}_2]$(2) and $[\{RhCl(C_2H_4)_2\}_2]$(3). It has also been shown that solid state vibrational spectroscopy is a useful tool to distinguish between both structures(4). This knowledge has led to the assumption that similar compounds with monodentate ligands have bent Rh_2L_2 (L = bridging ligand) rings, whereas those in which chelating ligands are involved, have a coplanar Rh_2L_2 entity(5, 6).

Several dinuclear transition metal compounds containing the bridging pentaflurothiophenolato-moiety are known(6, 7). Unfortunately the solid state structures have been resolved only for a limited number of compounds(7) and, to our knowledge, none of these is a rhodium derivative.

Our interest in dimeric rhodium compounds with bridging $(SC_6F_5)^-$ groups, prompted us to study further the validity of the above-mentioned structural assumption, which should have important implications regarding both chemical and stereoscopic aspects of these species.

The molecular structure and labeling scheme for $[\{Rh(SC_6F_5)(COD)\}_2]$ are shown in Figure 1*.

Two essentially planar $Rh(SC_6F_5)(COD)$ groups intersect at an angle of *ca.* 117°. With this geometry, the Rh–Rh bond length is 2.955 Å which is, not unexpectedly, outside the range found for similar compounds having a two-electron bond (2.40–2.50 Å)(8). This distance may be compared with those found in the carbonyl(2) (3.31 Å) and the ethylene(3) (3.498 Å) compounds, respectively.

Although the structure of $[\{Rh(SC_6F_5)(COD)\}_2]$ is similar to that of $[\{RhCl(CO)_2\}_2]$, there is no evidence of intramolecular interactions such as those present in the chloro-bridged compound, which explain the bending of the Rh_2Cl_2 ring.

Molecular models suggest that steric interactions could induce the adopted structure. Particularly noteworthy are the non-bonded distances between the *ortho*-fluorine and the

---

* Author to whom all correspondence should be directed.

* The atomic coordinates and full lists of bond lengths, bond angles and F_0/F_c values have been deposited as supplementary material with the Editor, from whom copies can be obtained on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

0340-4285/84/0707-0284$02.50/0