boxylates in the two axial positions; for Ca(2), a distorted pentagonal bipyramid with the bidentate carboxylate and four water molecules in equatorial positions and symmetry-related monodentate carboxylates axially disposed. The primary mode of bonding to the mellitate ring involves a four-membered chelate ring containing the calcium ion and both oxygen atoms of the carboxylate group. This mode of bonding is commonly found for calcium ion coordination to organic carboxylates; for example, it has previously been observed as the primary mode of calcium ion binding in calcium malate dihydrate,[15] calcium fumarate trihydrate,[16] and calcium terephthalate trihydrate.[5] The interaction of Ca^{2+} with a benzenepolycarboxylate containing ortho-related carboxylates (e.g., mellitate with two or less acid hydrogens[17]) might conceivably involve the formation of a seven-membered chelate ring containing Ca^{2+} and the two ortho-related carboxylates; this would require the rotation of the two carboxylates to suitable positions with a minimum of steric strain. Models can be constructed which indicate that the two carboxylates can be suitably placed without any restrictive steric interactions. However, evidence of such binding was not found in the structure of the Ca_2H_2mellitate crystal. We therefore prefer to believe that the four-membered ring formation involving the Ca^{2+} and a single carboxylate provides the most stable metal–ligand interaction in such a complex. The presence of seven-membered ring formation, of course, cannot be ruled out in aqueous solution and may well be involved as a (transition) state of binding in the rapidly exchanging Ca^{2+}–ligand solution system.

To the best of our knowledge, only one other Ca^{2+}–benzenecarboxylate (1:1) binding constant has been reported:[18] Ca^{2+}phthalate^{2-}, log K_{11} = 1.07 (IS = 0.15). The significantly larger value of log K_{11} = 3.05 (IS = 0.10) for Ca^{2+}mellitate^{6-} is not unexpected due to the higher charge of the anion and the presence of six carboxylates which are all equally available for binding with Ca^{2+} in the course of the rapid exchange processes occurring in aqueous solution. Perhaps an even stronger interaction might be expected between Ca^{2+} and a highly charged ligand such as mellitate^{6-} (pK_6 = 7.49). However, this charge is evenly distributed over a relatively large, probably highly hydrated molecule; and, apparent from the structural analysis of Ca_2H_2mellitate, the effectiveness of this charge with respect to binding Ca^{2+} cannot be augmented by suitable chelation as, for example, in the calcium complex of EDTA^{4-} [19] which has a stability constant of log K = 10.6.[20] It is of interest to compare the stability of the Ca^{2+}mellitate binding with that of Ca^{2+}oxydiacetate^{2-} which has a very similar 1:1 stability constant (log K = 3.4).[21] Relative to mellitate, the ODA anion is of considerably lower charge and contains fewer binding sites; however the stability of the CaODA complex is derived to a large degree from the ability to form two fused five-membered chelate rings involving both carboxylates and the ether oxygen atom.[14] In view of the characteristics of the mellitate anion (e.g., high charge and multiple, separated binding sites), in solutions of relatively high Ca^{2+} concentration the presence of complexes with more than one Ca^{2+} per ligand is also to be expected. In fact, in order to suitably fit the calcium electrode titration data it was necessary to assume, in addition to the 1:1 complex, the presence of a complex of stoichiometry Ca_2(mellitate)$^{2-}$ with a stability constant (K_{21} = 0.37 × 10^3) of a magnitude not greatly different from the 1:1 complex.

Acknowledgment. The authors wish to acknowledge the experimental assistance of M. Webb and D. Etson and very helpful discussions with Dr. W. A. Cilley of these laboratories.

Registry No. Ca_2H_2mellitate·$9H_2O$, 64189-25-9.

Supplementary Material Available: Listings of anisotropic thermal parameters (Table A-1), structure factor amplitudes (Table A-II), [Ca^{2+}] vs. emf standard curve (Figure A-1), and titration data containing [Ca^{2+}] and the average number of Ca^{2+} ions bound per ligand (Table A-III) (16 pages). Ordering information is given on any current masthead page.

---

(15) C-I. Brändén and B-O. Suderberg, *Acta Chem. Scand.*, **20**, 730 (1966).
(16) M. P. Gupta, S. M. Prasad, R. G. Sahu, and B. N. Sahu, *Acta Crystallogr., Sect. B*, **28**, 135 (1972).
(17) The assumption of symmetrical order of ionization[4] precludes ortho carboxylates if more than two acid hydrogen atoms are present on the mellitate species.
(18) N. R. Joseph, *J. Biol. Chem.*, **164**, 529 (1946).
(19) B. L. Barnett and V. A. Uchtman, *Inorg. Chem.*, **10**, 2674 (1979).
(20) J. H. Grimes, A. J. Huggard, and S. P. Wilford, *J. Inorg. Nucl. Chem.*, **25**, 1225 (1963).
(21) R. M. Tichane and W. E. Bennett, *J. Am. Chem. Soc.*, **79**, 1293 (1957).

Contribution from the Department of Chemistry,
University of Arizona, Tucson, Arizona 85721

Bis(dithiocarbamato)–Nitrosyl Complexes of Ruthenium

JULES V. DUBRAWSKI and ROBERT D. FELTHAM*

Received March 27, 1979

The synthesis of new dithiocarbamato complexes of ruthenium is reported including *trans*-[RuNO(S_2CNRR')$_2$Cl] (R = R' = Me, Et; R = Me, R' = Et; R = Me, R' = Ph), *trans*-[RuNO(S_2CNMe_2)$_2$OH]·CH_3OH, *trans*-[RuNO(S_2CNMe_2)$_2$$H_2O$]$BF_4$, *trans*-[RuNO($S_2CNMe_2$)$_2$$CH_3OH$]$PF_6$, *cis*-[RuNO($S_2CNMe_2$)$_2$X] (X = F, Br, I, NO_2), *cis*-[RuNO(S_2CNRR')$_2$X] (X = Br, I; R = R' = Et; R = Me, R' = Et), and *cis*- and *trans*-[RuNO(S_2CNMe_2)$_2$X] (X = N_3, SCN, NCO). In contrast with the iron complex, *cis*-Ru(NO)($^{15}NO_2$)(S_2CNMe_2)$_2$ does not undergo exchange between the NO and NO_2 ligands. The spectral characteristics of these complexes are discussed in relation to their geometric configuration. The ^{13}C NMR spectra of many of these complexes are reported and give valuable information regarding the bound ligand. The rotation of the unidentate dithiocarbamate ligand in *cis*-[RuNO(S_2CNMe_2)$_3$] is clearly differentiated from the two bidentate ligands.

Introduction

Sulfur ligands stabilize numerous nitrosyl complexes, but few sulfur derivatives of ruthenium nitrosyls have been reported. Those ruthenium complexes which are known include *cis*-Ru(NO)(S_2CNR_2)$_3$ (R = Me, Et),[1,2] *trans*-Ru(NO)(Cl)(SacSac)$_2$,[3] $RuX_3(NO)L_2$ (X = Cl, Br; L = Me_2S, Et_2S, PhEtS, PhMeS, (n-Pr)$_2$S, n-PrPhS),[4] and [$RuBr_3$(NO)-

---

(1) L. Cambi and L. Malatesta, *Rend. Ist Lomb. Sci. Lett., Cl. Sci. Mat. Nat.*, **71**, 118 (1938); *Chem. Abstr.*, **34**, 3201 (1940).

0020-1669/80/1319-0355$01.00/0

Table I. Properties of Nitrosyl-Dithiocarbamato Complexes of Ruthenium

complex	color	mp, °C dec	Λ_m, S cm^2 [a]
trans-[RuNO(S_2CNMe_2)$_2$Cl]	yellow	316–318	
trans-[RuNO(S_2CNEt_2)$_2$Cl]	yellow	187–189	2.6
trans-[RuNO($S_2CNMePh$)$_2$Cl]	yellow	227–229	
trans-[RuNO($S_2CNMeEt$)$_2$Cl]	yellow	246–248	1.7
trans-[RuNO(S_2CNMe_2)$_2N_3$]	yellow-orange	233–234	
trans-[RuNO(S_2CNMe_2)$_2$NCO]	yellow	268–270	
trans-[RuNO(S_2CNMe_2)$_2$SCN]	yellow	250–252	
trans-[RuNO(S_2CNMe_2)$_2$OH]·CH_3OH	amber	224–228	2.4
trans-[RuNO(S_2CNMe_2)$_2H_2O$]BF_4	yellow	178–180	76[b]
trans-[RuNO(S_2CNMe_2)$_2CH_3OH$]PF_6	yellow	134–137[f]	60
cis-[RuNO(S_2CNMe_2)$_3$]	deep red	218–220	0.3
cis-[RuNO(S_2CNMe_2)$_2$F]	brown	130–135[f]	17[h]
cis-[RuNO(S_2CNMe_2)$_2$Br]	gold-brown	248–249	3.9
cis-[RuNO(S_2CNMe_2)$_2$I]	black-brown	283–287	4.2
cis-[RuNO(S_2CNEt_2)$_2$Br]	brown	122–126	
cis-[RuNO(S_2CNEt_2)$_2$I]	black-brown	132–135	
cis-[RuNO($S_2CNMeEt$)$_2$Br]	brown	150–155	
cis-[RuNO($S_2CNMeEt$)$_2$I]	brown	146–149	
cis-[RuNO(S_2CNMe_2)$_2NO_2$]·$^1/_4CH_3OH$	light brown	200–202	4.3
cis-[RuNO(S_2CNMe_2)$_2N_3$]	light brown	232–233[d]	4.7
cis-[RuNO(S_2CNMe_2)$_2$SCN]	brown	250–252[d]	3.0
cis-[RuNO(S_2CNMe_2)$_2$NCO]	khaki	271–273[d]	
BP[e]	brown	209–214	3.6[c] (465[g])

[a] In CH_3NO_2; 1:1 complexes; Λ_m ~75–90 S cm^2. [b] In CH_3OH; 1:1 complexes; Λ_m ~80–115 S cm^2. [c] In DMF, 1:1 complexes; Λ_m ~65–90 S cm^2. [d] Isomerization to trans complex occurs. [e] Mixture of *cis*-[RuNO(Me_2NCS_2)$_3$] and *trans*-[RuNO(OH)(Me_2NCS)$_2$] in 2:1 ratio. [f] Impure complexes. [g] Molecular weight measured in $CHCl_3$ and extrapolated to zero concentration (concentration range 4.8–31.5 mg/mL). [h] Λ_m consistent with presence of aquo and methanol complexes.

$(Et_2SO)]_2$.[5] In addition to these nitrosyl species, $Ru^{III}(S_2CNR_2)_3$,[6,7] $Ru(CO)_2(S_2CNR_2)_2$ (R = Me, Et, $C_6H_5CH_2$),[8] $Ru(CO)(S_2CNR_2)_2$ (R = Me, Et),[8] $[Ru^{III}(S_2CN(CH_2Ph)_2)_2(CO)_2]Cl$,[8] and $[Ru_2(S_2CNEt_2)_5]BF_4$[9] and the seven-coordinate complexes of ruthenium(IV) $RuCl(S_2CNEt_2)_3$[10] and $Ru(S_2CNMe_2)_3I_3$[11] have been reported. More recently the chemical and electrochemical properties of new ruthenium(II), -(III), and -(IV) dithiocarbamato complexes have been described.[12] The related series of iron nitrosyl complexes $Fe(NO)(S_2CNR_2)_2$ (R = Me, Et, Ph),[13,14] $Fe(NO)(S_2CNMe_2)_2X$ (X = Br, I, NO_2, SCN), and $[Fe(NO)(S_2CNMe_2)_2X]Y$ (X = CH_3CN, CH_3NC, C_5H_5N; Y = BF_4, PF_6)[14] have been prepared and their reactions investigated. The observation[14,15] that *cis*-$Fe(NO)(S_2CNMe_2)_2(NO_2)$ undergoes a novel intramolecular oxygen exchange between the coordinated nitro and nitrosyl groups has prompted the present investigation.

Results

Synthesis and Reactions. The reaction between ruthenium nitrosyl trichloride and 2 equiv of dithiocarbamate ligand resulted in the exclusive formation of the trans isomers, *trans*-$Ru(NO)(S_2CNRR')_2Cl$ (where R = R′ = Me or Et; R′ = Et or Ph). Treatment of ruthenium nitrosyl trichloride in methanol with 3 equiv of sodium dimethyldithiocarbamate led to the formation of a less tractable brown material. Although this brown material was obtained consistently from this reaction, it is a mixture of $Ru(NO)(S_2CNMe_2)_3$ and *trans*-$Ru(NO)(S_2CNMe_2)_2(OH)$. The two components of this mixture were separated by chromatography and identified by comparison of their NMR spectra with authentic samples independently prepared. Refluxing this brown mixture or ruthenium nitrosyl trichloride with *excess* sodium dimethyldithiocarbamate resulted in the formation of deep red crystals of $Ru(NO)(S_2CNMe_2)_3$, a complex which has been prepared previously from the reaction of NO with $Ru(S_2CNMe_2)_3$.[1,2] This brown mixture also reacts with HF, HBr, and HI but not with H_2S to form the corresponding *cis*-$Ru(NO)(S_2CNMe_2)_2X$ complexes. However, except for the fluoro derivative, the other synthetic routes described below are superior. In this reaction, the fluoro complex was obtained in low yields and was accompanied by varying amounts of the aquo complex.

Reaction of any of the trans chloride complexes with HBr or HI produced the corresponding bromide or iodide complexes with cis geometry. Other derivatives with cis configurations were prepared by treatment of either *cis*-$Ru(NO)(S_2CNMe_2)_2I$ or *trans*-$Ru(NO)Cl(S_2CNMe_2)_2$ in methanol with AgX (where X = N_3, NCO, or NCS). Some *trans*-$Ru(NO)(S_2CNMe_2)_2(OH)$ was also formed in these reactions with AgX and was identified by direct preparation from the reaction of Ag_2O with *cis*-$Ru(NO)(S_2CNMe_2)_2I$. To obtain analytically pure materials, it was found necessary to purify each of these compounds by column chromatography.

In an attempt to isolate both cis and trans isomers of individual complexes, several solvates were prepared from *cis*-$Ru(NO)(S_2CNMe_2)_2I$ or *trans*-$Ru(NO)Cl(S_2CNMe_2)_2$ by using $AgBF_4$ or $AgPF_6$. These compounds include *cis*-$[Ru(NO)(S_2CNMe_2)_2(MeOH)][PF_6]$, *trans*-$[Ru(NO)(S_2CNMe_2)_2(H_2O)][BF_4]$, and $[Ru(NO)(S_2CNMe_2)_2(MeOH)][PF_6]$. Although this approach had limited success in that both cis and trans isomers of the azido, cyanato, and

---

(2) A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Commun.*, 476 (1966).
(3) G. A. Heath and R. L. Martin *Aust. J. Chem.*, **23**, 2297 (1970).
(4) C. T. Page and J. E. Fergusson, *Aust. J. Chem.*, **29**, 2159 (1976).
(5) J. E. Fergusson, C. T. Page, and W. T. Robinson, *Inorg. Chem.*, **15**, 2270 (1976).
(6) L. Malatesta, *Gazz. Chim. Ital.*, **68**, 195 (1938).
(7) L. Cambi and L. Malatesta, *Ber. Dtsch. Chim. Ges. A*, **70**, 2067 (1937).
(8) J. V. Kingston and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 2709 (1967).
(9) B. M. Mattson, J. R. Heinian, and L. H. Pignolet, *Inorg. Chem.*, **15**, 564 (1976).
(10) K. W. Given, B. M. Mattson, and L. H. Pignolet, *Inorg. Chem.*, **15**, 3152 (1976).
(11) B. M. Mattson and L. H. Pignolet, *Inorg. Chem.*, **16**, 488 (1977).
(12) S. H. Wheeler, B. M. Mattson, G. L. Miessler, and L. H. Pignolet, *Inorg. Chem.*, **17**, 340 (1978).
(13) H. Büttner and R. D. Feltham, *Inorg. Chem.*, **11**, 971 (1972); L. Cambi and A. Cagnasso, *Atti. Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat. Rend.*, **13**, 254, 809 (1931).
(14) O. A. Ileperuma and R. D. Feltham, *Inorg. Chem.*, **16**, 1876 (1977).
(15) O. A. Ileperuma and R. D. Feltham, *J. Am. Chem. Soc.*, **98**, 6039 (1976).

Table II. Analytical Results (Experimental Values in Parentheses)

complex	% C	% H	% N	% X	% O
trans-$[\mathrm{RuNO(S_2CNMe_2)_2Cl}]$	17.71 (17.65)	2.97 (2.70)	10.32 (10.23)	8.71 (9.00)	
trans-$[\mathrm{RuNO(S_2CNEt_2)_2Cl}]$	25.94 (25.45)	4.35 (4.06)	9.08 (8.91)	7.66 (7.70)	
trans-$[\mathrm{RuNO(S_2CNMePh)_2Cl}]$	36.18 (35.98)	3.04 (2.91)	7.91 (7.85)	6.67 (6.60)	
trans-$[\mathrm{RuNO(S_2CNMeEt)_2Cl}]$	22.09 (21.86)	3.71 (3.54)	9.66 (9.45)	8.15 (8.23)	
trans-$[\mathrm{RuNO(S_2CNMe_2)_2N_3}]$	17.43 (17.43)	2.93 (2.78)	20.32 (20.12)		
trans-$[\mathrm{RuNO(S_2CNMe_2)_2NCO}]$	20.33 (20.45)	2.93 (3.17)	13.55 (13.39)		
trans-$[\mathrm{RuNO(S_2CNMe_2)_2SCN}]$	19.57 (19.64)	2.82 (2.66)	13.04 (12.87)		
trans-$[\mathrm{RuNO(S_2CNMe_2)_2OH}]\cdot\mathrm{CH_3OH}$	19.99 (19.95)	4.08 (3.70)	9.99 (9.97)		11.41 (10.59)
trans-$[\mathrm{RuNO(S_2CNMe_2)_2H_2O}]\mathrm{BF_4}$	15.13 (15.09)	2.96 (3.30)	8.82 (8.55)		
trans-$[\mathrm{RuNO(S_2CNMe_2)_2CH_3OH}]\mathrm{PF_6}$	15.33 (14.20)	2.94 (3.02)	7.66 (7.19)		
cis-$[\mathrm{RuNO(S_2CNMe_2)_3}]$	21.98 (22.03)	3.69 (3.57)	11.39 (11.14)		
cis-$[\mathrm{RuNO(S_2CNMe_2)_2F}]$	18.45 (19.00)	3.10 (2.81)	10.76 (10.18)	4.87 (4.14)	
cis-$[\mathrm{RuNO(S_2CNMe_2)_2Br}]$	15.96 (16.06)	2.68 (2.55)	9.31 (9.18)	17.70 (18.00)	
cis-$[\mathrm{RuNO(S_2CNMe_2)_2I}]$	14.46 (14.63)	2.43 (2.21)	8.43 (8.19)	25.46 (25.37)	
cis-$[\mathrm{RuNO(S_2CNEt_2)_2Br}]$	23.67 (23.88)	3.97 (3.72)	8.28 (8.55)	15.74 (16.00)	
cis-$[\mathrm{RuNO(S_2CNEt_2)_2I}]$	21.66 (21.68)	3.64 (3.49)	7.58 (7.39)	22.89 (23.06)	
cis-$[\mathrm{RuNO(S_2CNMeEt)_2Br}]$	20.04 (20.19)	3.36 (3.15)	8.76 (8.66)	16.67 (16.90)	
cis-$[\mathrm{RuNO(S_2CNMeEt)_2I}]$	18.25 (18.51)	3.06 (2.88)	7.98 (7.70)	24.10 (24.30)	
cis-$[\mathrm{RuNO(S_2CNMe_2)_2NO_2}]\cdot{}^1/_4\mathrm{CH_3OH}$	17.64 (17.59)	3.08 (2.77)	13.17 (13.09)		12.22 (12.33)
cis-$[\mathrm{RuNO(S_2CNMe_2)_2N_3}]$	17.43 (17.70)	2.93 (2.87)	20.32 (20.27)		
cis-$[\mathrm{RuNO(S_2CNMe_2)_2SCN}]$	19.57 (19.84)	2.82 (2.56)	13.04 (12.82)		
cis-$[\mathrm{RuNO(S_2CNMe_2)_2NCO}]$	20.33 (20.59)	2.93 (2.68)	13.55 (13.27)		
$\mathrm{NaS_2CNMeEt\cdot 3H_2O}$	22.74 (22.49)	6.68 (5.97)	6.63 (6.37)		
BP[a]	21.01 (21.39)	3.60 (3.36)	11.23 (10.91)		4.67 (4.56)

[a] *cis*-$[\mathrm{RuNO(S_2CNMe_2)_3}]$ + *trans*-$[\mathrm{RuNO(S_2CNMe_2)_2OH}]$ (2:1).

thiocyanato complexes were isolated, this synthetic route normally led to mixtures of cis and trans isomers which had to be separated by column chromatography. An unusual and superior synthetic route for conversion of cis isomers to trans was fortunately discovered, however. Heating the solid cis azido, cyanato, and thiocyanato complexes in the temperature range from 160 to 210 °C resulted in rapid and quantitative conversion of the trans isomers to cis geometry as judged by infrared and NMR spectroscopy and by microanalysis. Some properties of the 22 isomerically pure compounds prepared in this study are listed in Table I. Their elemental analyses are set out in Table II.

One of the primary aims in this research was to explore the possible exchange reaction between NO and NO_2 ligands bound to ruthenium. Consequently, the ^{15}N-enriched and unenriched nitro complex *cis*-$\mathrm{Ru(NO)(S_2CNMe_2)_2(NO_2)}$ was prepared from the reaction of *cis*-$\mathrm{Ru(NO)(S_2CNMe_2)_2I}$ with $\mathrm{Ag^{15}NO_2}$ and $\mathrm{AgNO_2}$, respectively. Neither nitrito complexes nor the trans isomer was observed in these reactions. The oxygen atom transfer reaction reported for *cis*-$\mathrm{Fe(NO)(S_2CNMe_2)_2(NO_2)}$[14] was explored for the ^{15}N-labeled ruthenium complex. Even though the NO and NO_2 ligands occupy adjacent coordination sites in *cis*-$\mathrm{Ru(NO)(S_2CNMe_2)_2(^{15}NO_2)}$, the nitrosyl ligand maintained its isotopic integrity under all of the experimental conditions to which it was subjected. Refluxing the cis nitro complex in toluene for 8 h did not result in ^{15}N enrichment of the nitrosyl ligand. Photolysis in dichloromethane resulted only in the loss of the coordinated $^{15}NO_2$ ligand. Exchange was also not effected by the addition of $\mathrm{Fe(NO)(S_2CNMe_2)_2}$ to solutions of the labeled ruthenium complex.

The lowered reactivity of these ruthenium complexes compared with the iron complexes was not unexpected, since it is well-known that ruthenium complexes are kinetically more inert than iron complexes. Moreover, the $\{\mathrm{RuNO}\}^6$ species are among the most stable nitrosyl complexes which are known. However, $\{\mathrm{RuNO}\}^6$ do readily react with nucleophiles,[16] so that attack by the adjacent oxygen of the NO_2 ligand is not unreasonable. Neither the addition of a radical initiator ($\mathrm{Fe(NO)(S_2CNMe_2)_2}$) nor photolysis led to oxygen atom exchange, however, indicating that the necessary activated complex is probably inaccessible.

Infrared Spectra. The solid-state spectra contained a number of intense absorption bands arising principally from $\nu(\mathrm{NO})$, $\nu(\mathrm{CN})$, and certain vibrations of several substituted ligands (Table III). The nitrosyl stretching frequencies occurred in the range 1795–1870 $\mathrm{cm^{-1}}$. Splitting of $\nu(\mathrm{NO})$ was observed in a few cases and was attributed to crystal lattice effects since solutions of these complexes exhibited only a single nitrosyl absorption band. The value of $\nu(\mathrm{NO})$ for the trans isomer was approximately 20 $\mathrm{cm^{-1}}$ higher than that of the cis isomer for the series $[\mathrm{RuNO(S_2CNMe_2)_2X}]$ (X = N_3, NCO, NCS). Appreciable variation in $\nu(\mathrm{NO})$ occurred among the trans isomers, ranging from 1795 $\mathrm{cm^{-1}}$ for the hydroxo complex to 1870 $\mathrm{cm^{-1}}$ for the methanol species. These variations reflect the differing trans influences of the substituents. Sinitsyn and Zvyagintsev[16] reported the effects of the trans ligand upon $\nu(\mathrm{NO})$ and assumed that this was directly related to the strength of the Ru–NO bond. Later, Mercer et al.[17] broadened this study by examining the effect of the trans ligand upon $\nu(\mathrm{Ru–NO})$ in the series *cis*- and *trans*-$[\mathrm{RuNO(X)(NH_3)_4}]^{2+}$.

The $\delta(\mathrm{Ru–NO})$ and $\nu(\mathrm{Ru–NO})$ absorptions are usually weak[18,19] and no assignments were made. Since $\nu(\mathrm{Ru–NO})$ could not be assigned with certainty, $\nu(\mathrm{NO})$ was taken as the measure of the effect exerted by the trans ligand. For the dimethyldithiocarbamato complexes, the hydroxide ion had the strongest trans effect and methanol the weakest. The variation of $\nu(\mathrm{NO})$ with trans substituent was in general agreement with the trends previously reported.[16,17] In contrast the cis complexes showed little variation in $\nu(\mathrm{NO})$ since the ligand trans to NO is a dithiocarbamate sulfur atom in each case. Similar results have also been noted for *cis*-$\mathrm{RuNO(X)(AA)_2}$ (X = Cl, Br; AA = bpy, phen),[20] although a cis effect has been reported for other ruthenium nitrosyl complexes.[17,20]

The $\nu(\mathrm{CN})$ frequency of these complexes at ca. 1540 $\mathrm{cm^{-1}}$ is nearly independent of the substituent. It is shifted to higher

---

(16) N. M. Sinitsyn and O. E. Zvyagintsev, *Dokl. Akad. Nauk SSSR*, **145**, 109 (1962).

(17) E. E. Mercer, W. A. McAllister, and J. R. Durig, *Inorg. Chem.*, **5**, 1881 (1966).

(18) M. S. Quinby and R. D. Feltham, *Inorg. Chem.*, **11**, 2468 (1972).

(19) M. Quinby-Hunt and R. D. Feltham, *Inorg. Chem.*, **17**, 2515 (1978).

(20) J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 471, 2150 (1971).

(21) S. Pell and J. N. Armor, *Inorg. Chem.*, **12**, 873 (1973).

Table III. Infrared Spectra (cm^{-1}) of $[\mathrm{RuNO(S_2CNRR')_2X}]$ and $[\mathrm{RuNO(S_2CNRR')_2X}]\mathrm{Y}$ (KBr Pellets)[a]

complex	ν(NO)	ν(CN)	bands due to X	bands due to Y
trans-$[\mathrm{RuNO(S_2CNMe_2)_2Cl}]$	1825 s	1540 s		
	1805 ms, sp			
	(1845)[b]			
trans-$[\mathrm{RuNO(S_2CNEt_2)_2Cl}]$	1840 s	1510 s		
trans-$[\mathrm{RuNO(S_2CNMePh)_2Cl}]$	1835 s	1490 s		
trans-$[\mathrm{RuNO(S_2CNMeEt)_2Cl}]$	1835 s	1530		
	1805 sh			
	(1840)[b]			
trans-$[\mathrm{RuNO(S_2CNMe_2)_2N_3}]$	1820 s	1540 s	2050 s $\nu_a(\mathrm{N_3})$	
	1800 sh		1290 w $\nu_s(\mathrm{N_3})$	
	(1840)[b]			
trans-$[\mathrm{RuNO(S_2CNMe_2)_2NCO}]$	1820 s	1530	2110 s ν_a(NCO)	
	1805 ms, sp		1350 m, sp ν_s(NCO)	
	(1845)[b]		595 m δ(NCO)	
trans-$[\mathrm{RuNO(S_2CNMe_2)_2SCN}]$	1840 s	1540 s	2065 s ν(CN)	
			2090 s	
trans-$[\mathrm{RuNO(S_2CNMe_2)_2OH}]\cdot\mathrm{CH_3OH}$	1795 s	1530 s	$\left.\begin{array}{l}3500\text{ m, br}\\2785\text{ m, sp}\end{array}\right\}\nu(\mathrm{OH})$	
			1070 ms δ(Ru-OH)	
			475 m ν(Ru-OH)	
trans-$[\mathrm{RuNO(S_2CNMe_2)_2H_2O}]\mathrm{BF_4}$	1810 s	1540 s	3150 sh	1030 s
			3300 br, ms ν(OH)	1060 s
			3400 sh	1100 s
			3500 sh	
			1610 br, w δ(HOH)	
trans-$[\mathrm{RuNO(S_2CNMe_2)_2CH_3OH}]\mathrm{PF_6}$	1870 s	1550 s	3600 sh ν(OH)	840
			3450 ms, br	560 s
			1650 sh δ(OH)	
			1000 w	
			485 w	
cis-$[\mathrm{RuNO(S_2CNMe_2)_3}]$	1825 s	1535 s		
		1490 ms, sh		
cis-$[\mathrm{RuNO(S_2CNMe_2)_2F}]$	1800 s	1540 s		
cis-$[\mathrm{RuNO(S_2CNMe_2)_2Br}]$	1810 s	1540 s		
cis-$[\mathrm{RuNO(S_2CNMe_2)_2I}]$	1805 s	1535 s		
cis-$[\mathrm{RuNO(S_2CNEt_2)_2Br}]$	1810 s	1525 s		
cis-$[\mathrm{RuNO(S_2CNEt_2)_2I}]$	1800 s	1510 s		
cis-$[\mathrm{RuNO(S_2CNMeEt)_2Br}]$	1800 s	1520 s		
cis-$[\mathrm{RuNO(S_2CNMeEt)_2I}]$	1800 s	1520 s		
cis-$[\mathrm{RuNO(S_2CNMe_2)_2NO_2}]\cdot{}^1/_4\mathrm{CH_3OH}$	1805 s	1545 s	1310 s $\nu_s(\mathrm{NO_2})$	
			820 ms, sp $\delta(\mathrm{NO_2})$	
cis-$[\mathrm{RuNO(S_2CNMe_2)_2{}^{15}NO_2}]$	1805 s	1545 s	1360 s $\nu_a(\mathrm{^{15}NO_2})$	
			1290 s $\nu_s(\mathrm{^{15}NO_2})$	
			815 ms, sp $\delta(\mathrm{^{15}NO_2})$	
cis-$[\mathrm{RuNO(S_2CNMe_2)_2N_3}]$	1800 s	1540 s	$\left.\begin{array}{l}1995\text{ s}\\2010\text{ s, sh}\end{array}\right\}\nu_a(\mathrm{N_3})$	
			1275 m $\nu_s(\mathrm{N_3})$	
cis-$[\mathrm{RuNO(S_2CNMe_2)SCN}]$	1825 s	1550 s	2100 s ν(CN)	
cis-$[\mathrm{RuNO(S_2CNMe_2)_2NCO}]$	1800 s	1535 s	$\left.\begin{array}{l}2175\text{ s}\\2200\text{ sh}\end{array}\right\}\nu_a(\mathrm{NCO})$	
			1320 w ν_s(NCO)	
BP[c]	1800 s	1535 s	2760 m, sp ν(OH)	
		1480 sh	1070 m δ(Ru-OH)	
			480 w ν(Ru-OH)	

[a] Abbreviations used: br = broad, m = medium, ms = medium strong, s = strong, sh = shoulder, sp = sharp, w = weak. [b] Measured in $\mathrm{CH_2Cl_2}$. [c] Mixture of *cis*-$[\mathrm{RuNO(S_2CNMe_2)_3}]$ and *trans*-$[\mathrm{RuNO(S_2CNMe_2)_2OH}]$.

energy compared with the free ligand as a result of increased double-bond character upon coordination to the metal center.[22,23] The shoulder observed at 1480 cm^{-1} in *cis*-Ru(NO)$(\mathrm{S_2CNMe_2})_3$ was attributed to the unidentate dithiocarbamate ligand.

Various coordinating substituents produced characteristic absorption bands. The isomers of $\mathrm{RuNO(S_2CNMe_2)_2X}$ (X = $\mathrm{N_3}$, NCO, NCS) revealed prominent $\nu_a(\mathrm{N_3})$, ν_a(NCO), and ν(CN) absorptions between 2210 and 2000 cm^{-1}. However $\nu_s(\mathrm{N_3})$ and ν_s(NCO) were much weaker, and ν(CS) was not observed. Both the trans azido and cyanato complexes possessed higher ν_a and ν_s stretching frequencies than their cis analogues while the reverse was true for ν(CN) of the corresponding thiocyanato complexes. The value of ν(CN) suggested S coordination by the SCN ligand.[24] The bands above 1350 cm^{-1} in the isocyanato complexes are higher than ν_s of free NCO$^-$ and indicate N coordination by the ligand.[24] Isomerization of *cis*-$\mathrm{RuNO(S_2CNMe_2)_2X}$ (X = $\mathrm{N_3}$, NCO, NCS) to the trans isomers resulted in the loss of the ν(NO) and ν(X) vibrations of the cis isomers and the appearance of ν(NO) and ν(X) of the trans isomers.

Two of the three $\mathrm{NO_2}$ vibrations of the nitro complex were observed at 1310 cm^{-1} ($\nu_s(\mathrm{NO_2})$) and 820 cm^{-1} ($\delta(\mathrm{NO_2})$). In

---

(22) C. O'Connor, J. D. Gilbert, and G. Wilkinson, *J. Chem. Soc. A*, **84** (1969).

(23) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Nature* (*London*), **177**, 1042 (1966); *Suom. Kemistil. B*, **39**, No 2., 75 (1966).

(24) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed., Wiley-Interscience, New York, 1978.

Table IV. ^{1}H NMR Absorptions of $[\mathrm{RuNO(S_2CNMe_2)_2X}]$ (in $CDCl_3$) Relative to Me_4Si (Ppm)[a]

complex	-CH_3	-CH_2-	-C_6H_5	X	integratn
trans-$[\mathrm{RuNO(S_2CNMe_2)_2Cl}]$	3.34				
trans-$[\mathrm{RuNO(S_2CNEt_2)_2Cl}]$	1.43, 1.33, 1.23	3.95, 3.93, 3.83 3.80, 3.70, 3.67, 3.57			CH_3:CH_2 = 1.6:1
trans-$[\mathrm{RuNO(S_2CNMePh)_2Cl}]$	3.67		7.42		C_6H_5:CH_3 = 1.8:1
trans-$[\mathrm{RuNO(S_2CNMeEt)_2Cl}]$	1.23, 1.37, 1.48 3.33	3.60, 3.67, 3.72 3.77, 3.83, 3.92, 4.03			CH_3:CH_2 = 3.1:1
trans-$[\mathrm{RuNO(S_2CNMe_2)_2N_3}]$	3.36				
trans-$[\mathrm{RuNO(S_2CNMe_2)_2NCO}]$	3.36				
trans-$[\mathrm{RuNO(S_2CNMe_2)_2SCN}]$	3.35				
trans-$[\mathrm{RuNO(S_2CNMe_2)_2OH]\cdot CH_3OH}$	3.37			4.02 br s (OH)	
trans-$[\mathrm{RuNO(S_2CNMe_2)_2H_2O]BF_4}$[b]	3.50			3.18 br (H_2O)	
trans-$[\mathrm{RuNO(S_2CNMe_2)_2CH_3OH]PF_6}$[b]	3.52			3.32 CH_3, 3.17 br (OH)	*Me*$_2$NCS$_2$:*Me*OH = 4.1:1
cis-$[\mathrm{RuNO(S_2CNMe_2)_3}]$	3.22, 3.35, 3.38 (A) 3.58 (B)				A:B = 2.0:1
BP[c]	3.20, 3.34, 3.37 (A) 3.58 (B)				A:B = 3:1
cis-$[\mathrm{RuNO(S_2CNMe_2)_2F}]$	3.38, 3.35 (A) 3.23 (B)				A:B = 3:1
cis-$[\mathrm{RuNO(S_2CNMe_2)_2Br}]$	3.33, 3.28 (A) 3.22 (B)				A:B = 3.1:1
cis-$[\mathrm{RuNO(S_2CNMe_2)_2I}]$	3.35, 3.32, 3.27 (A) 3.23 (B)				A:B = 3.1:1
cis-$[\mathrm{RuNO(S_2CNEt_2)_2Br}]$	1.48, 1.45, 1.35 1.33, 1.25, 1.20, 1.13	complex multiplet–broadened 3.82, 3.72, 3.67 3.58, 3.53, 3.47			CH_3:CH_2 = 1.7:1
cis-$[\mathrm{RuNO(S_2CNEt_2)_2I}]$	1.47, 1.42, 1.33, 1.30 1.22, 1.18, 1.10	complex multiplet 3.88, 3.82, 3.77 3.67, 3.65, 3.55, 3.43			CH_3:CH_2 = 1.6:1
cis-$[\mathrm{RuNO(S_2CNMeEt)_2Br}]$	3.30, 3.27, 3.20 1.57, 1.43, 1.37, 1.32 1.25, 1.20, 1.13	complex multiplet 3.98, 3.87, 3.73 3.62, 3.50			CH_3:CH_3CH_2 = 1:1.7
cis-$[\mathrm{RuNO(S_2CNMeEt)_2I}]$	3.30, 3.27, 3.25, 3.20 1.43, 1.37, 1.32, 1.22 1.20, 1.18, 1.12	complex multiplet 3.85, 3.73 3.62, 3.45			CH_3:CH_3CH_2 = 1:1.8
cis-$[\mathrm{RuNO(S_2CNMe_2)_2NO_2]\cdot {}^1/_4CH_3OH}$	3.37, 3.35, 3.31 (A) 3.24 (B)				A:B = 3.2:1
cis-$[\mathrm{RuNO(S_2CNMe_2)_2N_3}]$	3.37, 3.36 (A) 3.24 (B)				A:B = 3.0:1
cis-$[\mathrm{RuNO(S_2CNMe_2)_2SCN}]$	3.37, 3.33, 3.30 (A) 3.19 (B)				A:B = 2.8:1
cis-$[\mathrm{RuNO(S_2CNMe_2)_2NCO}]$	3.35, 3.33 (A) 3.23 (B)				A:B = 3.1:1

[a] For *cis*-$[\mathrm{RuNO(S_2CNMe_2)_2X}]$, A:B refers to the ratio of the integrated intensities of peaks at lower field (A) to that of the peak at highest field (B). [b] CD_3COCD_3. [c] *cis*-$[\mathrm{RuNO(S_2CNMe_2)_3}]$ and *trans*-$[\mathrm{RuNO(S_2CNMe_2)_2OH}]$ in 2:1 ratio.

the ^{15}N labeled complex, ν_a was found at 1360 cm^{-1}. The observed NO_2 frequencies are indicative of N coordination by the nitro ligand.[24]

The hydroxo, aquo, and methanol complexes had characteristic OH frequencies. The hydroxo complex was characterized by a sharp peak at 2785 cm^{-1}, probably associated with hydrogen bonding to methanol, a strong δ(Ru–OH) band at 1070 cm^{-1} and a band at 475 cm^{-1} due to ν(Ru–OH). In *trans*-$[\mathrm{RuNO(OH)(NH_3)_4]X_2}$ (X = Cl, Br, I), δ(Ru–OH) and ν(Ru–OH) occur at approximately 965 and 560 cm^{-1}, respectively.[17] The aquo complex produced broad bands at approximately 3300 and 1610 cm^{-1}, due to asymmetric and symmetric ν(OH) and δ_a(HOH), respectively. The methanol complex produced absorptions similar to the aquo complex consistent with the spectra reported for several ethanol complexes prepared by Van Leeuwen.[25] The three weak bands at 1080, 1000, and 490 cm^{-1} were not assigned. If the solvent was not dried, the methanol complex was often found to be contaminated by the aquo species and the hydroxo complex resulting in an extra nitrosyl absorption near 1810 cm^{-1}. In view of these facts, the bands at 1080 and 490 cm^{-1} were attributed to the hydroxo complex, while that at 1000 cm^{-1} was due to coordinated methanol.

NMR Spectra. The ^{1}H NMR spectra (Table IV) of the trans dimethyldithiocarbamato complexes produced a single sharp signal, indicating the equivalence of the methyl groups. A triplet and quartet were observed for *trans*-Ru(NO)Cl(S_2CNEt_2)$_2$. In addition to the single CH_3 peak, the spectrum of *trans*-Ru(NO)(S_2CNMe_2)$_2$(OH)·CH_3OH has a slightly broadened resonance at 4.02 ppm due to the OH groups. The CH_3 group of the solvate molecule was not observed in the ^{1}H NMR spectrum but was found in the ^{13}C NMR spectrum (vide infra). The aquo complex produced a broad peak at 3.18 ppm due to coordinated water. Addition of HBF_4 to solutions of the hydroxo complex resulted in new peaks at 3.50 and 3.18 ppm, indicative of conversion to the aquo complex. Two signals in the ratio of 4:1 corresponding to the dithiocarbamato and methanol methyl groups of *trans*-$[\mathrm{RuNO(S_2CNMe_2)_2CH_3OH}]^+$ were observed at 3.52 and 3.32 ppm. A broad peak at 3.17 ppm was attributed to the OH group of CH_3OH.

The cis dimethyldithiocarbamato complexes showed a maximum of four resonances in the ^{1}H NMR spectra, due to four inequivalent methyl groups. In those cases where only three signals were observed for *cis*-RuNO(S_2CNMe_2)$_2$X (X = F, Br, N_3, NCO), the resonances at lowest field were approximately twice the intensity of each of the other two. The

---

(25) P. W. N. M. Van Leeuwen, *Recl. Trav. Chim. Pays-Bas*, **86**, 247 (1967).

Table V. ^{13}C NMR Absorptions Relative to Me_4Si (Ppm)

compd	assignmt			solvent
	$-CH_3$	$-CH_2$	$-C\langle$	
$NaS_2CNMe_2 \cdot 2H_2O$	45.1		211.6	CD_3OD
	45.8		208.1	D_2O
$NaS_2CNEt_2 \cdot 3H_2O$	12.4	49.5	206.5	D_2O
$NaS_2CNMeEt \cdot 3H_2O$	43.0, 11.9	52.5	207.3	D_2O
trans-$[RuNO(S_2CNEt_2)_2Cl]$	12.5	45.3	211.7	$CDCl_3$
trans-$[RuNO(S_2CNMeEt)_2Cl]$	37.0, 11.9	47.6	212.1	$CDCl_3$
trans-$[RuNO(S_2CNMe_2)_2OH] \cdot CH_3OH$	39.5, 53.4 (CH_3OH)		214.2	$CDCl_3$
trans-$[RuNO(S_2CNMe_2)_2N_3]$	39.8		213.3	$CDCl_3$
trans-$[RuNO(S_2CNMe_2)_2SCN]$	39.8		*a*	$CDCl_3$
trans-$[RuNO(S_2CNMe_2)_2H_2O]BF_4$	40.6		210.3	CD_3COCD_3
cis-$[RuNO(S_2CNMe_2)_2NO_2] \cdot {}^1/_4 CH_3OH$	40.1, 39.7, 39.1 38.3, 53.4 (CH_3OH)		208.3, 203.3	$CDCl_3$
cis-$[RuNO(S_2CNMeEt)_2I]$	36.7, 36.1, 35.9, 35.4 12.2, 12.0	47.3, 46,4 45.6	210.4, 202.1	$CDCl_3$
cis-$[RuNO(S_2CNEt_2)_2I]$	12.7, 12.5	44.9, 44.2, 43.4	210.0, 201.7	$CDCl_3$
cis-$[RuNO(S_2CNMe_2)_2I]$	39.2, 38.6, 38.5, 37.9		211.1, 202.7	$CDCl_3$
cis-$[RuNO(S_2CNMe_2)_2Br]$	39.3, 38.9, 38.8, 38.1		210.4, 203.4	$CDCl_3$
cis-$[RuNO(S_2CNMe_2)_2F]$[b]	46.9, 39.6, 39.3, 38.9, 38.4, 38.1		208.5, 202.1	$CDCl_3$
cis-$[RuNO(S_2CNMe_2)_2SCN]$	39.5, 39.2, 39.0, 38.2		*a*	$CDCl_3$
cis-$[RuNO(S_2CNMe_2)_2N_3]$	39.8, 39.4, 39.0, 38.2		210.4, 204.3	$CDCl_3$
cis-$[RuNO(S_2CNMe_2)_3]$	45.8, 44.3 br 39.4, 39.1, 39.0, 38.2		210.9, 205.9 203.9	$CDCl_3$
BP	45.9, 44.5 br 39.5, 39.3, 39.0 38.9, 38.1		214.2, 210.6 205.7, 203.7	$CDCl_3$
cis-$[FeNO(S_2CNMe_2)_2NO_2]$	39.5, 38.9, 38.5, 37.9		204.0, 202.2	$CDCl_3$

[a] Quaternary carbon resonances not observed. [b] Peaks due to methanol and to aquo complex also present.

spectra of the cis complexes indicated that at ambient temperature the dithiocarbamato ligand is essentially stereochemically rigid. The result of isomerizing *cis*-$RuNO(S_2CNMe_2)_2X$ (X = N_3, NCO, NCS) to the trans isomer was clearly evident in the ^{1}H and ^{13}C NMR spectra. The multiple methyl resonances of the cis isomers changed to a single peak indicative of the trans complexes. The ^{1}H NMR spectrum of *cis*-$[RuNO(S_2CNMe_2)_3]$ produced a strong signal at 3.58 ppm of half the area of the methyl resonances at higher field and was attributed to the methyl groups of the unidentate dithiocarbamate ligand.

The proton-decoupled ^{13}C NMR spectra (Table V) substantiated the isomeric assignments made from ^{1}H NMR and confirmed the stereochemical rigidity of the bidentate dithiocarbamato ligand at ambient temperatures. Single ^{13}C resonances were observed for the methyl, methylene, and quaternary carbons of the trans complexes. Being unenhanced by NOE, the signals of the quaternary carbons were much weaker than those of the other carbon atoms and consequently were more difficult to detect. However, in the presence of a paramagnetic species the T_1 relaxation time of quaternary carbon nucleii is decreased,[26-28] allowing detection without recourse to long pulse delays or very small flip angles. With ~0.1 mol dm^{-3} of $Cr^{III}(acac)_3$, significant enhancement of signal intensities was obtained with no observable contact shift (<0.1 ppm) and only modest line broadening. The poor solubility of *cis*- and *trans*-$Ru(NO)(S_2CNMe_2)_2(SCN)$ prevented observation of the quaternary carbon resonances even in the presence of chromium(III).

The cis dimethyldithiocarbamato complexes produced four methyl and two quaternary carbon peaks in each case. The spectrum of the fluoro complex showed three extra peaks which were due to the presence of the aquo and methanol impurities. The spectrum of *cis*-$RuNO(S_2CNMe_2)_3$ was interesting. Four methyl resonances were observed for the bidentate dithiocarbamates, and three peaks were seen for the quaternary carbons, one for each of the dithiocarbamate ligands in the molecule. By comparison with the other cis complexes, the peak at 205.9 ppm was assigned to the quaternary carbon of the unidentate ligand. In addition, two very broad resonances appeared at approximately 44 and 46 ppm resulting from the two methyl groups of the unidentate ligand, indicating slow rotation of the methyl groups and/or dithiocarbamato ligand. The brown product mentioned earlier gave a spectrum which was a composite of *cis*-$RuNO(S_2CNMe_2)_3$ and *trans*-$Ru(NO)(S_2CNMe_2)_2(OH)$ (see Table V).

The ^{1}H NMR spectrum of *cis*-$[RuNO(S_2CNMeEt)_2X]$ revealed a complex multiplet for the ethyl groups and four peaks of comparable intensity for the methyl groups (only three were seen for the bromo complex, one peak being more intense and unresolved). The ^{13}C NMR spectrum of the iodo complex revealed several peaks corresponding to the methyl and methylene carbons. The *N*-methyl-*N*-ethyldithiocarbamato ligand can coordinate about ruthenium to form four geometrically distinct species and thereby generate four magnetically discrete sites for each methyl or ethyl group. The ^{13}C NMR spectrum showed four distinct methyl and three methylene peaks (one of twice the intensity, indicating accidental superposition) together with two very close resonances at high field corresponding to the methyl carbons of the ethyl group. By contrast, *trans*-$Ru(NO)Cl(S_2CNMeEt)_2$ showed single peaks for all methyl and methylene carbons. As expected, the ^{1}H NMR spectrum of *cis*-$Ru(NO)(S_2CNEt_2)_2X$ (X = Br, I) was complex due to the several multiplets arising from four inequivalent methyl and methylene groups. The ^{13}C spectrum of the iodo derivative, however, produced three distinct methylene peaks (again with one of twice the intensity) and two methyl peaks similar to the spectrum of the *N*-methyl-*N*-ethyldithiocarbamato complex.

Electronic Spectra. Each of the complexes has intense absorption bonds in the ultraviolet region in the vicinity of 250–300 nm, $\epsilon > 10^4$ mol^{-1} dm^3 cm^{-1}. A very weak absorption

---

(26) O. A. Gansow, A. R. Burke, and G. N. LaMar, *Chem. Commun.*, 456 (1972).

(27) O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Am. Chem. Soc.*, **94**, (1972).

(28) D. F. S. Natusch, *J. Am. Chem. Soc.*, **93**, 2566 (1971).

Table VI. Electronic Spectra (in CH_2Cl_2)

complex	λ, nm (ε, $mol^{-1}\ dm^3\ cm^{-1}$)
$NaS_2CNEt_2 \cdot 3H_2O$[a]	257 (1.26×10^4), 290 (1.58×10^4)
trans-$[RuNO(S_2CNMe_2)_2Cl]$	270 (3.6×10^4), 290 (3.1×10^4), 555 sh (~20)
trans-$[RuNO(S_2CNEt_2)_2Cl]$	272 (3.6×10^4), 290 (3.3×10^4), 550 sh (~15)
trans-$[RuNO(S_2CNMePh)_2Cl]$	270 sh (3.2×10^4), 298 (4.3×10^4), 550 sh (~20)
trans-$[RuNO(S_2CNMeEt)_2Cl]$	271 (3.6×10^4), 291 (3.3×10^4), 555 sh (~10)
trans-$[RuNO(S_2CNMe_2)_2N_3]$	275 (4.0×10^4), 555 sh (~10)
trans-$[RuNO(S_2CNMe_2)_2NCO]$	270 (3.7×10^4), 555 sh (~15)
trans-$[RuNO(S_2CNMe_2)_2SCN]$	273 (3.7×10^4), 350 sh (4.5×10^3), 555 sh (~20)
trans-$[RuNO(S_2CNMe_2)_2OH] \cdot CH_3OH$	278 (4.0×10^4), 290 sh (3.1×10^4), 555 sh (~25)
trans-$[RuNO(S_2CNMe_2)_2H_2O]BF_4$[b]	223 (2.6×10^4), 276 (3.4×10^4)
trans-$[RuNO(S_2CNMe_2)_2CH_3OH]PF_6$[b]	223 (~3×10^4), 277 (~3×10^4), 550 br sh (~15)
cis-$[RuNO(S_2CNMe_2)_3]$	245 sh (3.3×10^4), 266 (4.1×10^4)
cis-$[RuNO(S_2CNMe_2)_2F]$	267 (~4×10^4), 294 sh (~2×10^4)
cis-$[RuNO(S_2CNMe_2)_2Br]$	268 (6.4×10^4), 310 sh (1.4×10^4), 550 sh (140)
cis-$[RuNO(S_2CNMe_2)_2I]$	258 (4.4×10^4), 270 (4.4×10^4), 550 br sh (230)
cis-$[RuNO(S_2CNEt_2)_2Br]$	243 sh (2.8×10^4), 270 (3.9×10^4), 310 sh (1.3×10^4), 550 sh (120)
cis-$[RuNO(S_2CNEt_2)_2I]$	260 (3.7×10^4), 275 (3.9×10^4), 555 br sh (230)
cis-$[RuNO(S_2CNMeEt)_2Br]$	245 (3.0×10^4), 269 (4.2×10^4), 300 sh (1.5×10^4), 540 sh (130)
cis-$[RuNO(S_2CNMeEt)_2I]$	255 sh (4.8×10^4), 270 (5.0×10^4), 550 sh (260)
cis-$[RuNO(S_2CNMe_2)_2NO_2] \cdot {}^1/_4 CH_3OH$	258 (4.0×10^4), 555 sh (55)
cis-$[RuNO(S_2CNMe_2)_2N_3]$	260 sh (3.6×10^4), 268 (3.8×10^4), 315 br sh (1.2×10^4), 560 sh (100)
cis-$[RuNO(S_2CNMe_2)_2SCN]$	255 sh (4.8×10^4), 270 (5.1×10^4), 550 br sh (100)
cis-$[RuNO(S_2CNMe_2)_2NCO]$	235 (2.6×10^4), 265 (4.1×10^4), 300 sh (1.7×10^4), 560 sh (70)

[a] Reference 35. [b] Recorded in methanol.

band was also seen at approximately 550 nm (Table VI). The ultraviolet absorptions most probably originate from ligand-centered transitions together with charge-transfer transitions between the ligands and metal center. A study[29] of dithioic acids assigned the high-energy absorptions to π–π^* transitions. It was not possible to differentiate between the cis and the trans isomers on the basis of the number of bands appearing in the spectrum. On the whole, the cis complexes were more deeply colored. In particular the shoulders at 550 nm of the visible region were stronger for the cis complexes since the tail end of the ultraviolet absorptions for these compounds extended considerably into the visible region of the spectrum.

These weak visible absorption bands compare favorably with the spectra[30] of *cis*- and *trans*-$[RuNO(X)(NH_3)_4]^{2+}$ (X = OAc, Cl, OH, NCO, N_3, Br) in which a weak band was observed at approximately 450 nm ($\epsilon \sim 20$ $mol^{-1}\ dm^3\ cm^{-1}$). Schreiner[30] assigned this absorption band to a composite of ${}^1A_1 \rightarrow [{}^3T_1, {}^3T_2]$ and $t_{2g} \rightarrow \pi^*NO$ transitions.

Discussion and Conclusions

These ruthenium–dithiocarbamato–nitrosyl complexes are air-stable compounds. The cis isomers are brown and the trans species yellow to amber. In keeping with the stability of other ruthenium nitrosyl complexes, the compounds are kinetically inert. It is probably the unique stability of the $\{RuNO\}^6$ moiety[31] which prevented oxygen atom transfer in *cis*-$RuNO(S_2CNMe_2)_2{}^{15}NO_2$.

The trans isomer is the thermodynamically favored product for almost half the complexes reported. The conversion of the kinetically formed *cis*-$Ru(NO)(S_2CNMe_2)_2X$ (X = N_3, NCO, NCS) to the trans isomer upon heating is in keeping with the cis to trans isomerization commonly observed for ruthenium nitrosyl ammine complexes.[32] However, many of the dithiocarbamato complexes could be isolated only with cis geometry: *cis*-$Ru(NO)(S_2CNRR')_2X$ (X = Br, I; R = R′ = Me or Et; R = Me, R′ = Et, and X = NO_2; R = R′ = Me). The chloro ligand differed from the other halo ligands in forming the trans isomer exclusively.

Some comparisons with the iron–dithiocarbamato system can be drawn.[13–15] In the main, the six-coordinate ruthenium complexes are more stable than their iron counterparts. For example the chloro and azido complexes of ruthenium are stable but all attempts to prepare the chloro or azido complexes of iron failed. The values of ν(NO) for the ruthenium complexes are comparable with the observed values for the six-coordinate iron compounds.

Although ${}^1H$ NMR spectroscopy readily distinguishes between the cis and trans configurations of the complexes, the ${}^{13}C$ NMR spectrum provided additional important information regarding the behavior of the entire dithiocarbamate ligand. This is particularly evident for *cis*-$Ru(NO)(S_2CNMe_2)_3$ where the ${}^1H$ NMR spectrum at room temperature exhibits a single peak for the two nonequivalent methyl groups of the monodentate dithiocarbamate ligand, while the ${}^{13}C$ NMR spectrum showed a slight splitting demonstrating their nonequivalence. The temperature dependence of the NMR spectrum of $Ru(NO)(S_2CNMe_2)_3$ was studied in the temperature range from −40 to +150 °C. The results show that the unidentate dithiocarbamate ligand has a low barrier to rotation (~14 kcal mol^{-1}) about the C–N bond and that there is no exchange between the unidentate and the two bidentate ligands over the temperature range investigated.

Experimental Section

Ruthenium nitrosyl trichloride purchased from Engelhardt was purified by twice fuming with hydrochloric acid until a red syrup was obtained. Drying over phosphorus pentoxide, in vacuo, resulted in a red solid. Dithiocarbamate ligands were used as purchased from Aldrich and Baker. Methylethylamine hydrochloride was used as received from Eastman. Ammonium *N*-phenyl-*N*-methyldithiocarbamate was prepared according to literature sources.[33,34] Column chromatography was carried out on Baker neutral alumina (pH 6–8).

Microanalyses were done by MHW Laboratories, Phoenix, Ariz., and Huffman Laboratories Inc., Wheatridge, Colo. Molecular weights were determined osmometrically by Huffman Laboratories, Inc. Solid infrared spectra were obtained from KBr pellets, using Perkin-Elmer

---

(29) M. L. Shankaranaryana and C. C. Patel, *Acta Chem. Scand.*, **19**, 1113 (1965).

(30) A. F. Schreiner, S. W. Lin, P. J. Hauser, E. A. Hopcus, D. J. Hamm, and J. D. Gunter, *Inorg. Chem.*, **11**, 880 (1972).

(31) Notation following J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974).

(32) F. Bottomley, *Coord. Chem. Rev.*, **26**, 7 (1978).

(33) *Beilstein, 4th ed.*, **12**, 237 (1950).

(34) O. A. Ileperuma, Ph.D. Thesis, University of Arizona, 1976.

(35) H. P. Koch, *J. Chem. Soc.*, 401 (1949).

Models 735 and 337. Melting point determinations, using a Thomas Hoover capillary melting point apparatus, were done in air and were uncorrected.

Electronic spectra were recorded by a Cary 14 spectrophotometer. Proton NMR spectra were measured in CH_2Cl_2, $CDCl_3$, or CD_3COCD_3 by using a Varian T-60 spectrometer. Broad-band-decoupled ^{13}C NMR spectra were recorded by using a Bruker WH-90. Molar conductances of 10^{-3} mol dm^{-3} solutions were determined by an Industrial Instruments conductivity bridge, Model RC-216B2.

trans-**[RuNO$(S_2CNRR')_2$Cl]. (a) R = R′ = Me.** Solid $NaS_2CNMe_2 \cdot 2H_2O$ (0.35 g) was added to a stirred methanolic solution (15 cm^3) of $RuNOCl_3 \cdot XH_2O$ (0.25 g). The initial red-violet solution quickly changed to brown with gradual deposition of a tan precipitate. After 30 min, the solid was collected and washed with a mixture of CH_3OH/CH_2Cl_2 leaving a yellow solid; yield 0.075 g, 20%. When the reaction was carried out by heating the reagents in methanol, followed by adding dilute HCl (~5 cm^3) and boiling, a higher yield of the complex was obtained (0.2 g, 50%). The complex was recrystallized from CH_2Cl_2/CH_3OH yielding yellow-orange needles.

(b) R = R′ = Et. Solid $NaS_2CNEt_2 \cdot 3H_2O$ (0.32 g) was added to a stirred methanolic solution of $RuCl_3NO \cdot XH_2O$ (0.18 g). After a deep brown coloration developed, concentrated HCl (1 cm^3) was added and the solution boiled. A yellow product was collected and washed with methanol (0.12 g, 36%). Recrystallization from CH_2Cl_2/CH_3OH gave yellow crystals.

(c) R = Me, R′ = Et. Addition of $NaS_2CNMeEt \cdot 2H_2O$ (0.41 g) to $RuCl_3NO \cdot XH_2O$ (0.25 g) in methanol gave a brown solution which yielded a yellow product upon addition of HCl and boiling (0.19 g, 45%). The complex was washed with water and methanol. Purification was achieved by passage of a CH_2Cl_2 solution of the complex though neutral alumina or by recrystallization from CH_2Cl_2/CH_3OH.

(d) R = Me, R′ = Ph. Addition of freshly prepared $NH_4S_2CNMePh$ (0.32 g) to a stirred methanolic solution of $RuNOCl_3 \cdot XH_2O$ (0.2 g) yielded a tan product. Washing with water, methanol, and ether left a yellow solid (0.06 g, 15%). Recrystallization from CH_2Cl_2/CH_3OH gave yellow crystals.

cis-**[RuNO$(S_2CNMe_2)_3$]/*trans*-[RuNO$(S_2CNMe_2)_2$OH].** (a) This mixture was isolated from the preparation of *trans*-[RuNO$(S_2CNMe_2)_2$Cl] provided the mother liquor was not acidified. After collection of the yellow complex, the brown filtrate deposited brown microcrystals on standing overnight (0.06 g, 16%).

(b) Refluxing 3 equiv of $NaS_2CNMe_2 \cdot 2H_2O$ (0.53 g) with $RuCl_3NO \cdot XH_2O$ (0.25 g) in methanol gave a brown solution and some insoluble trans-chloro complex. After filtration and refluxing for about 10 min, brown microcrystals were obtained on standing (0.18 g, 50%). Microanalysis and IR and NMR spectra of this brown material revealed that it contains bidentate and unidentate dithiocarbamate ligands (3:1) and a coordinated hydroxyl group. A molecular weight determination indicated the presence of monomeric species. The solutions were nonconducting (Table I). Chromatography of this brown mixture resulted in isolation of Ru(NO)$(S_2CNMe_2)_3$ and *trans*-Ru(NO)$(S_2CNMe_2)_2$(OH) in a ratio of 2:1. Comparison with a genuine sample of Ru(NO)$(S_2CNMe_2)_3$ indicates that it was present in the original mixture. The properties of the hydroxo complex isolated from the mixture were identical with those of an independently prepared sample.

cis-**[RuNO$(S_2CNMe_2)_3$].** Refluxing 0.1 g of brown product with a large excess of $NaS_2CNMe_3 \cdot 2H_2O$ (~0.2 g) in methanol yielded a red-brown solution. When the mixture was allowed to stand, deep red crystals appeared (0.05 g, 48%). These were collected and washed with methanol. Recrystallization was possible from CH_2Cl_2/CH_3OH.

cis-**[RuNO$(S_2CNRR')_2$Br]. (a) R = R′ = Me.** A suspension of *trans*-[RuNO$(S_2CNMe_2)_2$Cl] (0.1 g) in methanol was refluxed with excess HBr (48% soln) until a brown solution was obtained. Evaporation gave brown microcrystals. Column chromatographic purufication showed a single brown band. Recrystallization was accomplished from CH_2Cl/CH_3OH; yield 0.095 g, 85%. The complex was also isolated on boiling *cis*-[RuNO$(S_2CNMe_2)_3$] (yield 63%) or the brown product (yield 45%) with HBr in methanol.

(b) R = R′ = Et. A methanolic solution of *trans*-[RuNO$(S_2CNEt_2)_2$Cl] (0.05 g) was refluxed with excess HBr (48%) for 30 min. The brown solution was evaporated and the solid washed with water and ether. Recrystallization from CH_2Cl_2/CH_3OH gave light brown crystals (0.03 g, 55%).

(c) R = Me, R′ = Et. A methanolic solution of *trans*-[RuNO$(S_2CNMeEt)_2$Cl] (0.1 g) and excess HBr (48% soln) was refluxed for approximately 40–50 min. The brown solution gave a brown solid (0.09 g, 82%), which was washed with water and ether. It was purified by dissolving in a minimum volume of CH_2Cl_2 followed by passage through a neutral alumina column (12 in. × $^1/_2$ in.). A single brown band was eluted with CH_2Cl_2. Addition of CH_3OH to the brown effluent yielded brown crystals on standing.

cis-**[RuNO$(S_2CNRR')_2$I]. (a) R = R′ = Me.** Refluxing a suspension of *trans*-[RuNO$(S_2CNMe_2)_2$Cl] (0.16 g) with excess HI (48%) for several hours gave a dark brown mixture. A dark brown product was collected, washed with methanol, and recrystallized from CH_2Cl_2/CH_3OH; yield 0.17 g (90%). Boiling *cis*-[RuNO$(S_2CNMe_2)_3$] or the brown product with HI in methanol also yielded the same product (yield ~80%).

(b) R = R′ = Et. The *trans*-[RuNO$(S_2CNEt_2)_2$Cl] complex (0.05 g) was refluxed with excess HI (48%) for 30 min. Overnight evaporation gave brown crystals. Recrystallization was from CH_3OH/CH_2Cl_2; yield 0.04 g (68%).

(c) R = Me, R′ = Et. A methanolic solution of *trans*-[RuNO$(S_2CNMeEt)_2$Cl] (0.1 g) and excess HI (48% soln) was refluxed for 45 min. A dark brown solid was isolated and washed with water (0.1 g, 84%). Purification was achieved by dissolving the product in a minimum amount of CH_2Cl_2 followed by passage through a neutral alumina column (12 in. × $^1/_2$ in.). A single brown band was eluted. Addition of CH_3OH to the brown effluent gave brown crystals on standing.

cis-**[RuNO$(S_2CNMe_2)_2$F].** A sample of *cis*-[RuNO$(S_2CNMe_2)_3$] (0.07 g) was suspended in methanol in a plastic beaker. Excess HF (48% soln) was added and the mixture heated until the solid dissolved giving a brown solution. On cooling of the solution, a brown solid formed which was collected and washed with ether; yield 0.04 g, 72%. The product was extracted into CH_2Cl_2 to which CH_3OH was added. A brown microcrystalline solid was isolated. Treatment of the brown product in like manner gave the same solid.

cis-**[RuNO$(S_2CNMe_2)_2NO_2$]·$^1/_4$CH$_3$OH.** A suspension of *cis*-[RuNO$(S_2CNMe_2)_2$I] (0.01 g) and $AgNO_2$ (0.04 g) in methanol was refluxed for approximately 5–10 min. A color range from dark brown to tan occurred. Cooling and filtering yielded a golden brown solution which gave a light brown solid on evaporation (0.067 g, 80%). The product was redissolved in a minimum of CH_2Cl_2 and passed through an alumina column. A brown band was readily eluted with CH_2Cl_2, leaving a thin brown band unshifted at the top of the column. Methanol was added to the eluted fraction which gave brown crystals upon evaporation; yield 60%. The product was washed with ether. The unshifted band was readily eluted with methanol and identified as *trans*-[RuNO$(S_2CNMe_2)_2$OH]·CH_3OH (yield ~9%).

The labeled complex *cis*-[RuNO$(S_2CNMe_2)_2{}^{15}NO_2$] was prepared from $Ag^{15}NO_2$ (^{15}N 99%). In $CDCl_3$ the labeled complex revealed a ^{15}N resonance 87.8 ppm downfield from $Na^{15}NO_3$.

trans-**[RuNO$(S_2CNMe_2)_2H_2O$]BF$_4$.** To a methanolic suspension of the nitro complex (0.065 g) in a plastic beaker was added excess HBF_4 (48% soln) and the mixture heated until the complex dissolved, giving a yellow solution. On cooling of the solution, tiny yellow needles appeared. These were collected and washed with ether; yield 0.05 g, 70%.

trans-**[RuNO$(S_2CNMe_2)_2CH_3OH$]PF$_6$.** A suspension of the iodo complex (0.06 g) and $AgPF_6$ (0.06 g) in dissolved, dried methanol was heated for several minutes. A yellow suspension developed rapidly. Upon cooling and filtering of the solution, a yellow solution was obtained which yielded a yellow product upon evaporation. This was washed with ether; yield 0.06 g, 90%. Recrystallization from methanol gave yellow crystals. Refluxing *trans*-[RuNO$(S_2CNMe_2)_2$Cl] with $AgPF_6$ in dried methanol for about 30–60 min gave the same product; yield 72%.

trans-**[RuNO$(S_2CNMe_2)_2$OH]·CH$_3$OH.** A brown suspension of the iodo complex (0.1 g) and Ag_2O (0.07 g) was refluxed together in methanol for 15 min. The yellow-brown mixture was cooled and filtered, yielding a golden brown filtrate from which amber crystals were isolated; yield 0.065 g, 76%. Recrystallization was from CH_2Cl_2/CH_3OH.

[RuNO$(S_2CNMe_2)_2N_3$]. (a) Cis Isomer. A suspension of *cis*-[RuNO$(S_2CNMe_2)_2$I)] (0.1 g) and AgN_3 (0.04 g) was refluxed in methanol for about 5 min. A tan coloration developed. After cooling and filtering of the solution, a light brown solid was obtained from the filtrate; yield 0.07 g, 85%. Dissolution in CH_2Cl_2 and passage through a neutral alumina column gave a brown band, readily elutable with CH_2Cl_2. Methanol was added to the effluent and brown crystals were obtained on standing.

(b) Trans Isomer. (i) Refluxing *trans*-[RuNO(S_2CNMe_2)$_2$Cl] (0.09 g) and AgN_3 (0.08 g) in methanol for ~6 h gave a brown suspension. Filtration, followed by evaporation, gave a brown solid (0.05 g). This was dissolved in a minimum amount of CH_2Cl_2 and passed through neutral alumina (12 in. × 1/2 in.). The trans isomer was eluted with CH_2Cl_2 as a yellow band. Methanol was added, and orange needles were obtained on standing; yield 0.022 g (24%). A thin brown band of the hydroxo complex remained at the head of the column. When *trans*-[RuNO(S_2CNMe_2)$_2$Cl] was refluxed with AgN_3 for only 2 h, lower yields of the trans isomer were obtained (4%). The cis isomer was eluted second from the column (20%).

(ii) A more convenient preparation entailed heating solid *cis*-[RuNO(S_2CNMe_2)$_2N_3$] in air to a temperature of approximately 180 °C. At ca. 150 °C, the brown crystals changed to yellow. The sample was left at 170–180 °C for approximately 10 min. The yellow product was washed with diethyl ether.

[RuNO(S_2CNMe_2)$_2$SCN]. (a) Cis Isomer. The method described for the azido complex was followed. The yield of product from 0.06 g of *cis*-[RuNO(S_2CNMe_2)$_2$I] and 0.025 g of AgSCN was 0.045 g, 85%. Dissolution in CH_2Cl_2 and passage through an alumina column showed only traces of trans isomer (pale yellow band) which eluted first. The cis isomer was present as a brown band. Recrystallization from CH_2Cl_2/CH_3OH gave brown crystals.

(b) Trans Isomer. Solid *cis*-[RuNO(S_2CNMe_2)$_2$SCN] was heated in air to approximately 220 °C. At 210–215 °C, a color change from brown to tan occurred. Under the microscope the product appeared as tiny yellow crystals. The sample was left at 220 °C for about 10 min. The product was then washed with ether and recrystallized from CH_2Cl_2/CH_3OH.

Poor yields of the complex were obtained by refluxing *trans*-[RuNO(S_2CNMe_2)$_2$Cl] (0.1 g) with AgSCN (0.09 g) in methanol for 4 h. The brown product (0.09 g) obtained after filtration was treated as for the cis isomer. The trans isomer was eluted first (4%) followed by the cis complex (15%). The trans hydroxo complex remained at the head of the column.

[RuNO(S_2CNMe_2)$_2$NCO]. (a) Cis Isomer. (i) A mixture of *cis*-[RuNO(S_2CNMe_2)$_2$I] (0.1 g) and AgNCO (0.05 g) was refluxed in methanol for 10 min. A color change from brown to yellow occurred. A yellow-brown solid was isolated after filtration. Dissolution in CH_2Cl_2 and passage through neutral alumina gave a light brown band which was readily eluted with CH_2Cl_2. Khaki crystals were obtained; yield 0.015 g, 18%. A second yellow band, not shifted by CH_2Cl_2, was readily eluted with CH_3OH and yielded amber crystals of *trans*-[RuNO(S_2CNMe_2)$_2$OH]·CH_3OH; yield 0.015 g, 18%.

(ii) Heating *cis*-[RuNO(S_2CNMe_2)$_2$I] (0.1 g) in acetonitrile with a slight excess of $AgPF_6$, followed by cooling and filtering, gave a yellow-orange solution. Solid KNCO (0.05 g) was added and a brown solution resulted after boiling the mixture for several minutes. The solid was treated as in (i). The yellow trans isomer was eluted first (5%) followed by the cis isomer (25%).

(b) Trans Isomer. Heating solid *cis*-[RuNO(S_2CNMe_2)$_2$NCO] in air to approximately 175 °C resulted in quantitative conversion to the yellow trans isomers. The product was washed with ether.

Sodium *N*-Methyl-*N*-ethyldithiocarbamate. *N*-Methyl-*N*-ethylamine hydrochloride (1 g) was dissolved in chilled methanol (10 cm^3). Addition of CS_2 (1 cm^3) was followed by an aqueous solution of NaOH (1 g in a minimum volume). Stirring gradually gave a yellow solution which upon slow evaporation yielded white crystals. These were collected, washed with ether and pentane, and recrystallized twice from methanol. The mother liquor yielded several batches of crystals: total yield 1.4 g, 64%; mp 113–115 °C.

Silver Salts. These were prepared by metathesis from silver nitrate and the required sodium salt. The labeled nitrite, $Ag^{15}NO_2$, was prepared from $AgClO_4$ and $Na^{15}NO_2$ (^{15}N 99%); yield 76%.

Acknowledgment. The authors wish to thank the National Science Foundation for support of this research. We also thank Dr. M. Barfield and Dr. D. Gust for their assistance in obtaining ^{15}N and ^{13}C NMR spectra.

Registry No. *trans*-[RuNO(S_2CNMe_2)$_2$Cl], 72075-88-8; *trans*-[RuNO(S_2CNEt_2)$_2$Cl], 72075-89-9; *trans*-[RuNO($S_2CNMePh$)$_2$Cl], 72075-90-2; *trans*-[RuNO($S_2CNMeEt$)$_2$Cl], 72075-91-3; *trans*-[RuNO(S_2CNMe_2)$_2N_3$], 72075-92-4; *trans*-[RuNO(S_2CNMe_2)$_2$NCO], 72075-93-5; *trans*-[RuNO(S_2CNMe_2)$_2$SCN], 72075-94-6; *trans*-[RuNO(S_2CNMe_2)$_2$OH], 72075-95-7; *trans*-[RuNO(S_2CNMe_2)$_2H_2O$]BF_4, 72075-97-9; *trans*-[RuNO(S_2CNMe_2)$_2CH_3OH$]PF_6, 72075-99-1; *cis*-[RuNO(S_2CNMe_2)$_3$], 51139-59-4; *cis*-[RuNO(S_2CNMe_2)$_2$F], 72076-00-7; *cis*-[RuNO(S_2CNMe_2)$_2$Br], 72076-01-8; *cis*-[RuNO(S_2CNMe_2)$_2$I], 72076-02-9; *cis*-[RuNO(S_2CNEt_2)$_2$Br], 72076-03-0; *cis*-[RuNO(S_2CNEt_2)$_2$I], 72076-04-1; *cis*-[RuNO($S_2CNMeEt$)$_2$Br], 72076-05-2; *cis*-[RuNO($S_2CNMeEt$)$_2$I], 72076-06-3; *cis*-[RuNO(S_2CNMe_2)$_2NO_2$], 72076-07-4; *cis*-[RuNO(S_2CNMe_2)$_2N_3$], 72120-76-4; *cis*-[RuNO(S_2CNMe_2)$_2$SCN], 72120-77-5; *cis*-[RuNO(S_2CNMe_2)$_2$NCO], 72120-78-6; $RuNOCl_3$, 18902-42-6.

Contribution from the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Novel Transition-Metal Complexes of Camphorquinone Dioxime Ligands

MAN SHEUNG MA and ROBERT J. ANGELICI*

Received June 25, 1979

Camphorquinone dioxime, H_2CQD, is known to exist in four isomeric forms (α, β, γ, and δ) which differ by the orientations of the OH groups on their oxime nitrogen atoms. The deprotonated β-$HCQD^-$ coordinates via the two N atoms to form the square-planar complexes Pd(β-HCQD)$_2$, Pt(β-HCQD)$_2$, and Cu(β-HCQD)$_2$·H_2O·$^1/_2$dioxane. However, δ- and α-$HCQD^-$ coordinate via one N and one O atom to yield square-planar complexes of the type Pd(δ-HCQD)$_2$, Ni(δ-HCQD)$_2$, and Ni(α-HCQD)$_2$. The neutral β-H_2CQD ligand forms Pd(β-H_2CQD)Cl_2, Pt(β-H_2CQD)Cl_2, and Cu(β-H_2CQD)Cl_2 complexes in which the ligand coordinates through both N atoms. Spectroscopic evidence indicates that α-, γ-, and δ-H_2CQD are monodentate ligands, coordinating via only one N atom, in Pd(α-H_2CQD)$_2Cl_2$, Pd(α-H_2CQD)$_2Cl_2$, and Pd(γ-H_2CQD)$_2Cl_2$. Finally, structures for two complexes of the unusual composition Ni(δ-HCQD)$_2$(δ-H_2CQD)$_2$ and [Pt(γ-HCQD)(γ-H_2CQD)Cl]$_2$ have been suggested. Ultraviolet–visible, infrared, ESR, and ^1H NMR spectroscopy were employed to characterize these new types of α-dioxime complexes.

Introduction

The chemistry of transition-metal complexes with α-dioxime ligands has been well studied and is the subject of several reviews.[1-5] Yet little was known about the coordination chemistry of transition metals with the camphorquinone dioxime ligands, H_2CQD, until last year when work in this laboratory[6] and in Osaka University[7-9] was reported.

---

(1) Chakravorty, A. *Coord. Chem. Rev.* **1974**, *13*, 1.

(2) Holm, R. H.; O'Connor, M. J. *Prog. Inorg. Chem.* **1971**, *14*, 277.

(3) Schrauzer, G. N. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 417.

(4) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 100.

(5) Thomas, T. W.; Underhill, A. E. *Chem. Soc. Rev.* **1972**, *1*, 99.

(6) Ma, M. S.; Angelici, R. J.; Powell, D.; Jacobson, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 7068.

(7) Nakamura, A.; Konishi, A.; Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3443.

0020-1669/80/1319-0363$01.00/0