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Identification of New Chromium(III) Nitrito Complexes by Means of the Electronic Spectrum of the Nitrito Ligand in Dipolar Aprotic Solvents[1a]

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Two new dinitritobis(ethylenediamine)chromium(III) complexes have been synthesized and isolated as the salts *cis*-$[Cr(en)_2(ONO)_2]ClO_4$ and *trans*-$[Cr(en)_2(ONO)_2]Z$ ($Z = ClO_4, NO_3$). Their infrared spectra and reflectance spectra are reported, as well as their ultraviolet–visible absorption spectra in water and in dimethylformamide. Normal infrared and electronic spectral criteria used to distinguish nitrito and nitro linkage isomers in cobalt(III) complexes have not been unequivocally applicable to the assignment of the new chromium(III) complexes as dinitrito complexes. An additional distinguishing criterion, applicable to the new complexes and based on electronic spectral differences of organic nitro compounds and alkyl nitrites, is proposed for transition metal complexes where absorption by the remaining metal–ligand moiety in the region 300–400 mμ is not strong. In an appropriate dipolar aprotic solvent, nitrito complexes give sharply resolved absorption bands in this region from the –ONO ligand, whereas the nitro isomers do not.

Introduction

Where both nitro ($M-NO_2$) and nitrito ($M-ONO$) linkage isomers of a transition metal (M) complex are known, as is the case with Co(III), Ni(II), Rh(III), Ir(III), and Pt(IV) compounds, the distinction of one isomer from the other is fairly readily achieved on the bases of infrared bands of the nitrito or nitro ligand and the energies of the metal d–d bands.[2] Where, however, only one of the linkage isomers is known and there is no guarantee that the spectrochemical series established for another metal will hold, then identification of the isomer from electronic spectral measurements of the kind normally applied to nitro *vs.* nitrito linkage assignments is inconclusive.

With Cr(III), only nitrito compounds have yet been identified. Although the spectrochemical series for Co(III),[3] which places the nitro group between *o*-phenanthroline and cyanide ion, and the nitrito group with a much weaker ligand field close to hydroxide and formate ions, seems generally applicable to Cr(III), the behavior of the d^3 Cr(III) and d^6 Co(III) central ions toward a π-acceptor ligand, such as the nitro ligand, may well be different. Hence, the formulation of nitritopentaamminechromium(III) chloride, *e.g.*, as a nitrito compound is mainly dependent upon the interpretation of its infrared spectrum,[4] despite the claim of Linhard, Siebert, and Weigel[5] that the ultraviolet–visible absorption spectrum is consistent with chromium–oxygen coordination. The neutral complex 1,2,3-trinitritotriamminechromium(III), synthesized and assigned as a trinitrito complex by Nakahara[6] on the basis of its visible reflectance spectrum, could presumably be characterized as a nitrito complex from its infrared spectrum.

In connection with an aquation kinetics investigation, two new dinitrito complexes have been synthesized and characterized, namely, *cis*- and *trans*-dinitritobis(ethylenediamine)chromium(III) cations as perchlorate and certain other salts. Neither of the above spectroscopic criteria could be unequivocally applied to the assignment of these complexes as dinitrito complexes. Fortunately, a third criterion for distinguishing nitro and nitrito isomers of transition metal complexes has been developed, based upon the electronic spectrum in dipolar aprotic solvents. In this paper we report this method, as well as the synthesis, characterization, and properties of the above two new dinitrito complexes of chromium(III).

Experimental Section

Preparation of Known Compounds.—The compounds $[Cr(NH_3)_5ONO](NO_3)_2$,[7] $[Co(NH_3)_5ONO](NO_3)_2$,[8] *trans*-$[Co(en)_2(NO_2)_2]NO_3$,[9,10] *trans*-$[Cr(en)_2Br_2]Br \cdot HgBr_2$,[11] and $[Cr(en)_3]Cl_3$[12] were prepared by procedures given in the literature. Thermal deamination of $[Cr(en)_3]Cl_3$ in a NaCl matrix[13] was used to prepare *cis*-$[Cr(en)_2Cl_2]Cl$, which was converted to the perchlorate salt by recrystallization from cold water upon addition of $HClO_4$ or $NaClO_4$. The methods of Woldbye[11] were used to synthesize

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[2] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **3**, 1389 (1964). This reference contains a summary of the evidence for distinguishing between nitro and nitrito linkage isomers, based upon these two criteria, for complexes of all the above-mentioned transition metals.

[3] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, London, New York, Paris, 1962, p 109.

[4] K. Nakamoto, J. Fujita, and H. Murata, *J. Am. Chem. Soc.*, **80**, 4817 (1958).

[5] M. Linhard, H. Siebert, and M. Weigel, *Z. Anorg. Allgem. Chem.*, **278**, 287 (1955). Their conclusion was based upon the similarity of the ultraviolet–visible spectrum to that of $Co(NH_3)_5ONO^{2+}$ and did not exclude the possibility of rapid isomerization from a nitro form during the preparation of the compound or its solutions.

[6] M. Nakahara, *Bull. Chem. Soc. Japan*, **35**, 785 (1962).

[7] M. Mori, *Inorg. Syn.*, **5**, 131 (1957). Mori described the product as $[Cr(NH_3)_5NO_2](NO_3)_2$; the strong acid conditions used imply the nitrito complex should form, and in our hands his method gave $[Cr(NH_3)_5ONO](NO_3)_2$, as confirmed by its infrared spectrum.

[8] F. Basolo and R. K. Murmann, *ibid.*, **4**, 171 (1953). In our hands the method gave $[Co(NH_3)_5ONO](NO_3)_2$, as confirmed by its infrared spectrum.

[9] H. F. Holtzclaw, Jr., D. P. Sheetz, and B. D. McCarty, *ibid.*, **4**, 176 (1953).

[10] The abbreviation en is used for ethylenediamine.

[11] F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958).

[12] M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **271**, 115 (1952).

[13] W. W. Wendlandt and C. H. Stembridge, *J. Inorg. Nucl. Chem.*, **27**, 575 (1965).

cis- and *trans*-$Cr(en)_2(OH_2)_2^{3+}$ salts from *cis*-$[Cr(en)_2Cl_2]ClO_4$, except that *cis*-$[Cr(en)_2(OH_2)_2](ClO_4)_3$ was obtained by substituting $HClO_4$ for HBr in the final step, and in the precipitation of the intermediate compound *trans*-$[Cr(en)_2(OH_2)OH]Br_2$ LiBr was used in place of KBr to increase the yield and eliminate contamination with KBr.[14] The compounds $[Cr(NH_3)_5ONO](ClO_4)_2$, $[Co(NH_3)_5ONO](ClO_4)_2$, and *trans*-$[Co(en)_2(NO_2)_2]ClO_4$ were made from the nitrate salts by dissolving in water and pouring onto solid $LiClO_4 \cdot 3H_2O$, filtering, washing with ethanol, and drying by suction and then over P_2O_5. Their infrared spectra showed them to be the indicated compounds. The compound *cis*-$[Co(NH_3)_4(ONO)_2]ClO_4$ was prepared from *cis*-$[Co(NH_3)_4CO_3]NO_3$,[15] which was converted to *cis*-$[Co(NH_3)_4(OH_2)_2](ClO_4)_3$ by trituration with just enough 12 *F* $HClO_4$ to make a paste, which was dissolved in a small volume of water at 0°, then solid $NaNO_2$ was added, and, after it dissolved, cold 12 *F* $HClO_4$ was added, giving a precipitate which was filtered after 30 min, washed with ethanol, and dried over P_2O_5. The nitro compounds $[Co(NH_3)_5NO_2](ClO_4)_2$ and *cis*-$[Co(NH_3)_4(NO_2)_2]ClO_4$ were made in 0.5-g lots by heating the corresponding nitrito compounds at 80° for 1 hr and at 70° for 2 hr, respectively (*caution*[16]). All commercially available compounds used were reagent grade, except anhydrous $CrCl_3$, which was Diamond Alkali Co. technical grade. Some $CrCl_3$ was made by heating Cr powder in Cl_2 at *ca.* 800° for 5–8 hr.

***trans*-Dinitritobis(ethylenediamine)chromium(III) Perchlorate.**—*trans*-$[Cr(en)_2(OH_2)_2]Br_3$ (2 g) was dissolved in the minimum volume (*ca.* 5 ml) of 20–25° distilled water and 2 drops of glacial acetic acid added. The solution was poured onto 1 g of finely ground anhydrous $LiNO_2$, then cooled in an ice bath for 10 min with stirring to ensure complete dissolution of the $LiNO_2$. The orange precipitate of *trans*-$[Cr(en)_2(ONO)_2]NO_2$ obtained was filtered off, washed with 50 ml of 20–25° absolute ethanol, and dried by suction. The nitrite salt was dissolved in the minimum volume (*ca.* 15 ml) of 20–25° distilled water and poured onto 1 g of finely ground $LiClO_4$ (or an equivalent amount of $LiClO_4 \cdot 3H_2O$). After cooling in an ice bath for 15 min with stirring, the orange precipitate of *trans*-$[Cr(en)_2(ONO)_2]ClO_4$ was filtered off, washed with 100 ml of absolute ethanol, then with 50 ml of ether, and dried over P_2O_5 in a vacuum desiccator in the dark for 24 hr. The product is a bright orange, finely crystalline solid; yield, 1 g (60%).

Anal. Calcd for $[Cr(en)_2(ONO)_2]ClO_4$: C, 13.2; H, 4.4; N, 23.1; Cr, 14.3; NO_2^-, 25.3. Found: C, 13.4; H, 4.3; N, 22.9; Cr, 14.5; NO_2^-, 25.2. A test for free nitrite gave a negative result.

The salt chars slowly at 240°, rapidly at 260°, and explodes at 270° (*caution*[16]); we do not recommend drying it by heating. It does not appear to be hygroscopic.

If the acetic acid is omitted in the above procedure the final product obtained is a pale orange, the different color presumably being due to a difference in particle size, since this product gave essentially the same chemical analyses and visible absorption spectrum as the above bright orange perchlorate salt.

***trans*-Dinitritobis(ethylenediamine)chromium(III) Nitrate.**—This salt was made by pouring a solution of 0.5 g of *trans*-$[Cr(en)_2(ONO)_2]ClO_4$ in 15 ml of water onto a slight excess of solid $NaNO_3$, stirring thoroughly, filtering off the precipitate, washing with 50 ml of ethanol and 25 ml of ether, then sucking dry and letting it stand in a desiccator over P_2O_5. The product is a bright orange crystalline substance; yield, 50%.

Anal. Calcd for $[Cr(en)_2(ONO)_2]NO_3$: C, 14.7; H, 5.0; N, 30.1; Cr, 16.0; NO_2^-, 28.2. Found: C, 14.7; H, 5.0; N, 28.9; Cr, 16.1; NO_2^-, 28.2.

This salt was not tested for explosive characteristics. Its visible absorption spectrum was the same as for the perchlorate salt.

***trans*-Dinitritobis(ethylenediamine)chromium(III) Chloride.**—This salt was prepared the same way as for the nitrate salt, except that LiCl was used in place of $NaNO_3$. The product is a dull orange; yield, 50%. No chemical analyses were made on it.

***cis*-Dinitritobis(ethylenediamine)chromium(III) Perchlorate.**—*cis*-$[Cr(en)_2(OH_2)_2](ClO_4)_3$ (1 g) was dissolved in the minimum volume (*ca.* 5 ml) of 20–25° distilled water and 3 drops of glacial acetic acid added. The solution was quickly cooled to <5°, and 1 g of powdered anhydrous $LiNO_2$ was added with vigorous stirring, giving a deep orange-red solution. Addition of 1 g of powdered anhydrous $LiClO_4$ with stirring, followed by cooling for 15 min in an ice bath, gave a bright orange-red precipitate of *cis*-$[Cr(en)_2(ONO)_2]ClO_4$, which was filtered off, washed, and dried as for the *trans* compound; yield, 0.3 g (40%).

Anal. Calcd for $[Cr(en)_2(ONO)_2]ClO_4$: Cr, 14.3; NO_2^-, 25.3. Found: Cr, 14.2; NO_2^-, 25.2.

The compound turns a deep red at 160° and chars within 30 sec at 210°; it explodes at 220° after 5 sec, at 230° after 2 sec, and instantly at 250° (*caution*[16]). We recommend drying the preparations only at room temperature. The compound does not appear to be hygroscopic.

***cis*-Dinitritobis(ethylenediamine)chromium(III) Nitrite.**—This salt can be precipitated in the procedure above by adding in place of 1 g of $LiNO_2$ enough $LiNO_2$ to saturate the *cis*-diaquo solution. It was washed and dried as for the *trans* nitrate salt, giving a bright orange-red solid; yield, 30%. No chemical analyses were made. Its visible absorption spectrum is essentially the same as that of the perchlorate salt, after correction for absorption by the free nitrite anion.

Attempts to precipitate chloride, bromide, and iodide salts of the *cis* complex by addition of the solid Na^+ or Li^+ halide to aqueous solutions of *cis*-$[Cr(en)_2(ONO)_2]ClO_4$ in the presence of excess $LiNO_2$ (to reduce the extent of aquation) were unsuccessful.

All chromium complexes were stored in the dark.

Organic Solvents.—Dimethyl sulfoxide (Matheson Coleman and Bell or By-Products and Chemicals Pty. Ltd. "Unilab") was dried by stirring over powdered BaO at 60°, decanting off, distilling at 20 torr, and taking the middle 70%. N,N-Dimethylformamide (B.D.H. Laboratory Grade) was used without further purification.

Analytical Methods.—Chromium compounds were analyzed for Cr by boiling with alkaline peroxide, making up to a standard volume, and measuring the optical absorbancy of the resulting CrO_4^{2-} solution at 372 mμ. Nitrite was determined by the method of Rao and Pandalai,[17] using 0.0015 *F* $Na_2S_2O_3$ standardized against KIO_3, except that O_2-free N_2 was used to remove O_2 and exclude air. The acid conditions in this determination are sufficient to release all coordinated nitrite well before the titration end point. To test for the possible presence of uncoordinated nitrite in *trans*-$[Cr(en)_2(ONO)_2]ClO_4$, an aqueous solution of the complex was charged onto a Na^+ Dowex AG50W-X8 (100–200 mesh) column to adsorb all the complex, and the column was washed with water to elute any free NO_2^-; titration revealed the absence of NO_2^- in this wash. Carbon, hydrogen, and nitrogen were determined by standard microanalytical procedures in the Microanalytical Laboratories at the University of California, Los Angeles, and the University of Melbourne; the explosive nature of the perchlorate salts restricted the number of such analyses which were performed.

Spectral Measurements.—Chromium analyses *via* CrO_4^{2-} absorbancy readings and all accurate molar absorbancy index measurements were made at 20–25° with a Beckman DU spectrophotometer (University of California, Los Angeles) or with a Shimadzu QR 50 or Unicam SP 500 spectrophotometer (Melbourne), with water in the reference cell. Reflectance spectra were taken on Beckman DK-2A and Unicam SP 800 recording spectrophotometers with reflectance attachments (Melbourne).

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(14) Contamination with KBr is difficult to remove except by reprecipitation of the complex as the very insoluble iodide salt, which is unsuitable for our purpose.

(15) G. Schlessinger, *Inorg. Syn.*, **6**, 173 (1960).

(16) Perchlorate compounds of this type are potentially or actually explosive, and should be heated only in small amounts behind a safety shield.

(17) G. G. Rao and K. M. Pandalai, *Analyst*, **59**, 99 (1934).

Ultraviolet–visible absorption spectra of solutions were taken at 20–25° in 1.00- or 10.00-cm silica cells on a Cary Model 11 recording spectrophotometer (University of California, Los Angeles) or on a Shimadzu SV 50A recording spectrophotometer (Melbourne), with the reference cell filled with water.

All infrared spectra were taken in KCl disks on Perkin-Elmer Model 421 spectrophotometers. Nujol mull spectra similarly taken showed that in no case did any detectable replacement of nitrito ligand by chloride occur in the KCl disks.

Results

Infrared Spectra.—Free nitrite ion has three fundamental vibrational modes, all active in the infrared region, with frequencies (cm^{-1}) of 1328 (antisymmetric stretch, ν_{as}), 1261 (symmetric stretch, ν_s), and 828 (bending mode, δ) in sodium nitrite.[18,19] Although the number of bands due to nitrate alone is not expected to change on coordination as nitrito or nitro, studies on nitrito and nitro transition metal complexes indicate[2] that ν_{as} usually increases in frequency in both –ONO and $-NO_2$ complexes relative to free NO_2^-, δ changes little, and ν_s decreases in frequency in –ONO complexes (strong band) and increases in $-NO_2$ complexes (weak band). An extra band, associated with the $-NO_2$ wagging mode, ρ_w, is expected to appear in nitro, but not in nitrito, complexes at about 580–630 cm^{-1}.[4] The previously known pentaammine complexes given in Table I show this behavior.

TABLE I

ACIDO LIGAND VIBRATION FREQUENCIES FOR *cis*- AND *trans*-$[Cr(en)_2(ONO)_2]ClO_4$ COMPARED WITH THOSE FOR SIMILAR NITRITO AND NITRO COMPLEXES (KCl DISK)[a]

Complex	ν_{as},[b] cm^{-1}	ν_s,[b] cm^{-1}	δ,[b] cm^{-1}	ρ_w,[b] cm^{-1}
trans-$[Cr(en)_2(ONO)_2]ClO_4$	1485, 1430	?	825, 835	...
cis-$[Cr(en)_2(ONO)_2]ClO_4$	1483	?	825, 835	...
$[Cr(NH_3)_5ONO](ClO_4)_2$	1470	1030	838	...
$[Co(NH_3)_5ONO](ClO_4)_2$	1456	1040	820	...
$[Co(NH_3)_5NO_2](ClO_4)_2$	1425	1307	820	589

[a] All complexes prepared and spectra taken in this research; values for the previously known pentaammine complexes agree well with literature values (see ref 4). [b] ν_{as} = antisymmetric stretch; ν_s = symmetric stretch; δ = bending vibration; ρ_w = $-NO_2$ wagging mode.

Infrared spectra of the two new nitrito complexes were examined over the region 2000–200 cm^{-1}, and the band assignments given for them in Table I were made by comparison with the spectra of $[Cr(en)_3]Cl_3$, *cis*-$[Cr(en)_2Cl_2]ClO_4$, *trans*-$[Cr(en)_2Br_2]Br$, $[Cr(NH_3)_5ONO](ClO_4)_2$, $[Co(NH_3)_5ONO](ClO_4)_2$, *cis*-$[Co(NH_3)_4(ONO)_2]ClO_4$, *cis*-$[Co(NH_3)_4(NO_2)_2]ClO_4$, and $[Co(NH_3)_5NO_2](ClO_4)_2$ examined under the same conditions. The first three compounds were used to distinguish bands due to coordinated ethylenediamine and perchlorate anion.

Bands due to Cr–N vibrations[20] were observed in *trans*-$[Cr(en)_2(ONO)_2]ClO_4$ at 558, 537 (very weak), 498, and 450 cm^{-1}, and in *cis*-$[Cr(en)_2(ONO)_2]ClO_4$ at 550, 533 (doublet), 485, 431, and 412 cm^{-1} (doublet). Because of their low symmetry, the *cis* complexes are expected to have more bands in this region, and this behavior was noted not only for these bis(ethylenediamine) compounds, but also for *cis*-$[Cr(en)_2Cl_2]Cl$ when compared with *trans*-$[Cr(en)_2Br_2]Br \cdot HgBr_2$.

Solution Electronic Spectra.—The near-ultraviolet–visible absorption spectra of sodium nitrite in water, N,N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) are given in Figure 1, and the absorption spectra of *cis*- and *trans*-$[Cr(en)_2(ONO)_2]ClO_4$ in water and in DMF in Figures 2 and 3, respectively.[21]

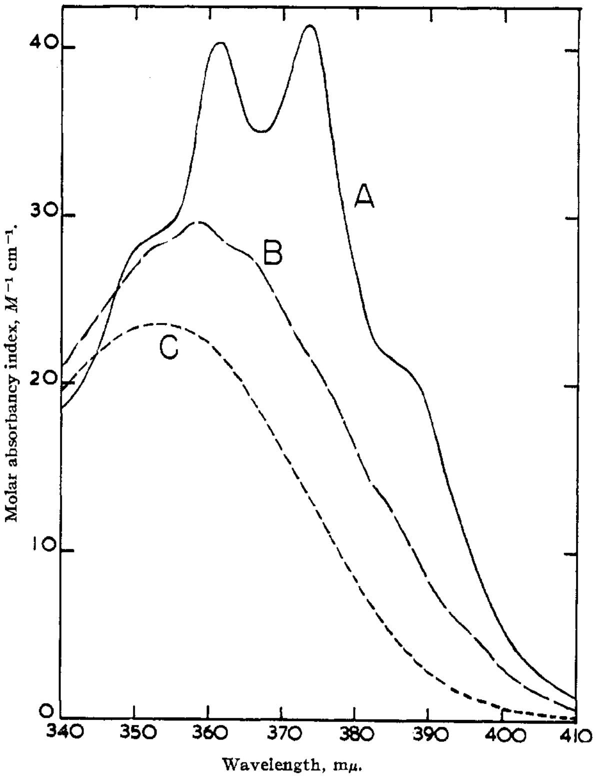

Figure 1.—Electronic spectra of sodium nitrite at 20–25°: A, in DMSO; B, in DMF; C, in H_2O.

Since the *cis* isomer aquates rapidly in aqueous solution at pH 6 and 25°, the spectrum given for it is an extrapolation to zero time of repeated spectral scans made at known short time intervals and may not be an accurate spectrum of the species *cis*-$Cr(en)_2(ONO)_2^+$.

Reflectance Electronic Spectra.—Reflectance spectra of the solid perchlorate salts and solid sodium nitrite are exhibited in Figure 4.

Discussion

Infrared Spectra.—A band clearly assignable to a nitrito symmetric stretching frequency (expected in the 1020–1070-cm^{-1} region)[22] could not be found in the infrared spectrum of either *cis*- or *trans*-$[Cr(en)_2(ONO)_2]ClO_4$ although there was an indication of absorption in the expected region in both cases (Table I).

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(18) R. E. Weston and T. F. Brodasky, *J. Chem. Phys.*, **27**, 683 (1957).

(19) J. Chatt, L. A. Duncanson, B. M. Gatehouse, J. Lewis, R. S. Nyholm, M. L. Tobe, P. F. Todd, and L. M. Venanzi, *J. Chem. Soc.*, 4073 (1959).

(20) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, London, 1963, pp 146–150, 186–189.

(21) Perchlorate salts of these and related Co(III) complexes are much more soluble in DMF and DMSO than the nitrate salts.

(22) Reference 20, p 155.

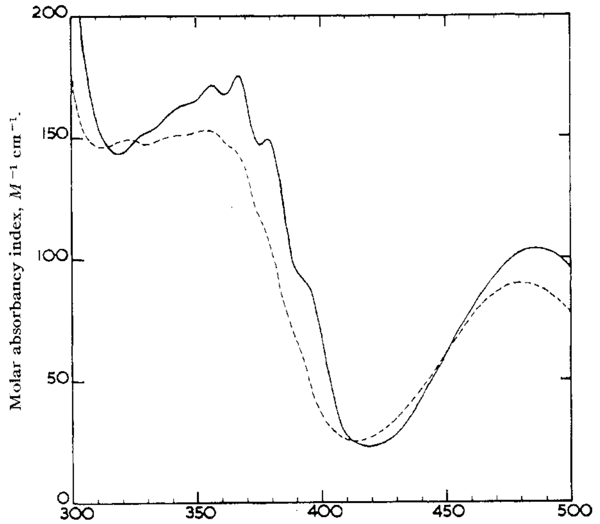

Figure 2.—Solution electronic spectra of *cis*-[Cr(en)$_2$(ONO)$_2$]-ClO$_4$ at 20–25°: ———, in DMF; - - - -, in H_2O, pH 6, extrapolated to t = 0.

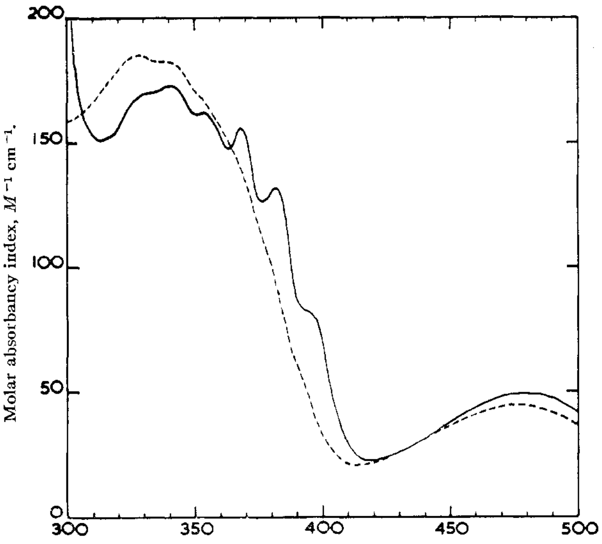

Figure 3.—Solution electronic spectra of *trans*-[Cr(en)$_2$(ONO)$_2$]-ClO$_4$ at 20–25°: ———, in DMF; - - - -, in H_2O, pH 6.

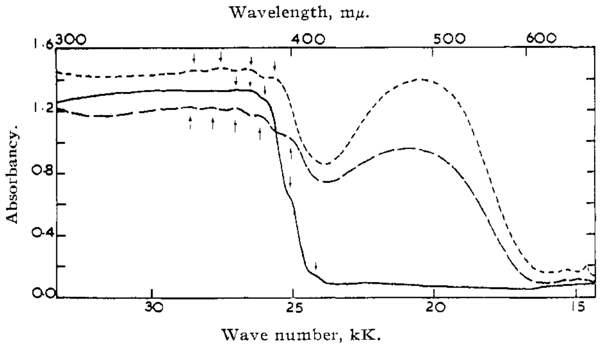

Figure 4.—Reflectance spectra at 20–25°: ———, $NaNO_2$; — — —, *trans*-[Cr(en)$_2$(ONO)$_2$]ClO$_4$; - - - -, *cis*-[Cr(en)$_2$-(ONO)$_2$]ClO$_4$.

However, this apparently weak absorption was overlaid by ethylenediamine bands and to some extent by perchlorate bands (1070–1200 cm^{-1}). Even when the *trans* compound was converted to the chloride salt to eliminate the perchlorate bands, the ethylenediamine bands remained to obscure a possible ν_s nitrito absorption. With all previously known nitrito complexes the –ONO ν_s band has been strong and readily detectable. The absence of a band assignable as a nitro wagging mode, ρ_w, not obscured by other bands, is incompatible with assignment of the two new complexes as dinitro or nitritonitro[23] complexes.

The Cr–N vibration bands (see Results) in the infrared spectrum of the complex to which we have assigned a *cis*-dinitrito geometric configuration exhibit splitting, whereas the other (*trans*) complex shows no splitting of these bands, as would be expected from the lower symmetry of the Cr–N skeleton in the *cis* isomer.

Electronic Spectra.—As pointed out in the Introduction, use of the spectrochemical series in distinguishing nitrito and nitro complexes is reasonably satisfactory where *both* isomers exist. In the pentaamminecobalt(III) series, the order of increasing ligand field is ONO < OH_2 < NO_2. In the diacidobis(ethylenediamine)cobalt(III) series, the order for both *cis* and *trans* isomers is $(OH_2)_2$ < $(ONO)_2$ < $(NO_2)_2$, although comparison in the *trans* series is rendered somewhat uncertain because of the large tetragonal distortion in the diaquo compound. Since Cr(III) nitro complexes are unknown, spectrochemical identification of nitrito complexes would require that a ligand X (or AA) be found for Co(III) fitting the series $(ONO)_2$ < (X_2) (or AA) < $(NO_2)_2$. For *trans* complexes ethylenediamine makes a convenient AA, but ethylenediamine does not fit for the *cis* complexes because the order is en < $(ONO)_2$ < $(NO_2)_2$. Hence, even though the ligand field for nitro is always greater than that for nitrito, certain identification of the linkage isomer spectrochemically does not appear possible when only the one isomer is known. Illustration of the problem may be seen from the near-ultraviolet–visible absorption spectral data for *cis*- and *trans*-Cr(en)$_2$(ONO)$_2{}^+$, given in Table II, together with the absorption spectra of some related cations.

Table II illustrates another possible electronic spectral distinction between nitrito and nitro complexes. The charge-transfer band II (which normally occurs at slightly shorter wavelength than the 353-mμ band of free nitrite ion) appears to have an intensity enhanced considerably over that of band I, especially in the nitro isomers. This increased band intensity for –NO_2 presumably lies in the strength of metal–ligand interaction, and since extensive organic chemistry studies have shown –NO_2 is a very effective electron-withdrawing group, it is not unexpected that –NO_2 may interact strongly with the metal ion. Again, however, this criterion is of limited use when only one of the two linkage isomers is known, as is the case for Cr(III).

Clearly a criterion for distinguishing nitro and nitrito isomers is needed which is applicable to the new

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[23] R. G. Pearson, P. M. Henry, J. G. Bergmann, and F. Basolo, *J. Am. Chem. Soc.*, **76**, 5920 (1954). Nitritonitro linkage was reported in *cis*-[Co(en)$_2$(ONO)NO$_2$]NO$_3$.

TABLE II

NEAR-ULTRAVIOLET AND VISIBLE ABSORPTION MAXIMA OF SOME HEXAAMMINE, NITRITO, AND NITRO COMPLEXES OF Cr(III) AND Co(III) IN AQUEOUS SOLUTION AT 15–25°

Complex	λ_{max} (I), mμ[a]	λ_{max} (II), mμ[a]
$Cr(NH_3)_6^{3+}$ [b]	464 (41.7)	351 (37.2)
$Cr(NH_3)_5ONO^{2+}$ [b]	482 (42.7)	356 (79.4)
cis-$Cr(en)_2(ONO)_2^+$ [c,d]	481 (90)	357 (152)
trans-$Cr(en)_2(ONO)_2^+$ [c]	477 (44)	328 (185)
$Co(NH_3)_6^{3+}$ [b]	475 (60.3)	339 (55)
$Co(NH_3)_5ONO^{2+}$ [b]	491 (72.4)	361 (275)
$Co(NH_3)_5NO_2^{2+}$ [b]	458 (100)	325 (1660)
cis-$Co(en)_2(ONO)_2^+$ [e]	455 (135)	
trans-$Co(en)_2(ONO)_2^+$ [e]	515 (55)	
cis-$Co(en)_2(ONO)NO_2^+$ [f]	464 (120)	
cis-$Co(en)_2(NO_2)_2^+$ [f]	441 (160)	
cis-$Co(en)_2(NO_2)_2^+$ [g]	437 (178)	322 (3900)
cis-$Co(en)_2(NO_2)_2^+$ [e]	435 (178)	
trans-$Co(en)_2(NO_2)_2^+$ [g]	430 (186)	342 (3550)
trans-$Co(en)_2(NO_2)_2^+$ [e]	430 (188)	

[a] Numbers inside parentheses are molar absorbancy indices a_M (extinction coefficients ϵ) in M^{-1} cm^{-1}, defined by the relation $A = \log (I_0/I) = a_M cd$, where c is the molarity of the complex and d is the optical path in cm. [b] Ref 5. [c] This research. [d] Based on extrapolation to zero time of spectral scans taken at known short time intervals; *cis*-dinitrito complex is aquating rapidly. [e] B. Adell, *Acta Chem. Scand.*, **5**, 54, 941 (1951). [f] Ref 23. [g] A. V. Ablov, T. A. Mal'kova, and E. V. Popa, *Russ. J. Inorg. Chem.*, **5**, 1305 (1960).

Cr(III) complexes. We propose the following considerations.

The low-energy electronic spectrum of free nitrite ion in aqueous solution at pH $\geqslant 6$ shows two weak bands at 353 mμ ($a_M = 24\ M^{-1}$ cm^{-1}) and 300 mμ ($a_M = 8\ M^{-1}$ cm^{-1}) and one intense band at 210 mμ ($a_M = 5440\ M^{-1}$ cm^{-1}). On the basis of the energy-level diagram and discussion given by Ballhausen and Gray[24] these can be assigned as follows: $^1A_1 \rightarrow {}^1B_2$ $[\ldots(4a_1)^2 \rightarrow \ldots(4a_1)^1(2b_2)^1]$, $^1A_1 \rightarrow {}^1A_2$ $[\ldots(3b_1)^2(4a_1)^2 \rightarrow \ldots(3b_1)^1(4a_1)^2(2b_2)^1]$, and $^1A_1 \rightarrow {}^1B_1$ $[\ldots(1a_2)^2(3b_1)^2(4a_1)^2 \rightarrow \ldots(1a_2)^1(3b_1)^2(4a_1)^2(2b_2)^1]$. The 353-mμ $^1A_1 \rightarrow {}^1B_2$ transition is the one of relevance here as it essentially involves the excitation of an electron, initially found as one of the lone pair on nitrogen, to the antibonding π orbital, roughly localized on the same atom. The low intensity of the band is due to its being forbidden by local symmetry, the orbitals being approximately at right angles to one another. On this basis, if the nitrogen lone pair becomes concerned in strong σ bonding as in nitro complexes (or in complexes containing bridging nitrite with $-O-N<^{O}$ bonding[25]), the energy of this transition will be markedly altered and hence no absorption around 350 mμ should occur, provided that other energy levels are little affected. For nitrito compounds, on the other hand, this absorption would be expected.

This, in fact, is what has been observed in the case of organic nitro compounds and alkyl nitrites, respectively. Altshuller, Cohen, and Schwab[26] have summarized a large amount of electronic spectral data on alkyl nitrites and include references to similar studies on nitro compounds. Together these data allow the conclusion, on empirical grounds alone, that it is a general rule that aliphatic nitro compounds show no absorption maximum above 300 mμ,[27] whereas alkyl nitrites invariably have a weak absorption maximum between 300 and 400 mμ. Altshuller, *et al.*, also suggest a similar assignment for the alkyl nitrite band to that above. The differentiation is made even more striking by the appearance of marked vibrational splittings in this weak band. This splitting persists even in aqueous solution and is, of course, well known in the case of R = H (nitrous acid, HONO). We have observed both the band and its fine structure in *cis*- and *trans*-$[Cr(en)_2(ONO)_2]ClO_4$, as well as in several known inorganic nitrito complexes, as discussed below. To the authors' knowledge, neither this electronic band nor its fine structure had been definitely observed in the electronic spectrum of any previously known inorganic nitrito complex.

The above rule for the distinction of coordination in organic systems holds provided the R group has no absorption maximum above 300 mμ. This was so with all the organic compounds studied,[26] but for transition metal systems there may be difficulty in detecting the nitrito band because the remaining metal–ligand moiety corresponding to R generally does absorb in this region. Fortunately, its vibronic structure affords a means of "tagging" the band even when it is overlaid by others. It will be noted that when describing the spectrum of nitrite ion in water above, no mention of fine structure in the 353-mμ band was made, and in fact no fine structure can be detected in water. However, by using dipolar aprotic solvents such as DMF and DMSO, resolution becomes possible (see Figure 1). The spectrum of sodium nitrite in DMSO is only slightly less well resolved than that of nitrous acid in water. It therefore seems certain that some form of solvent interaction, perhaps only that specifically with the nitrogen lone pair, affects both the intensity and resolution of the nitrite band. Thus, to optimize conditions for the observation of the band in inorganic nitrito complexes, the use of solvents such as DMF and DMSO seems advisable.

Both *cis*- and *trans*-$Cr(en)_2(ONO)_2^+$ cations were found to undergo fairly rapid reaction, presumably solvolysis, in DMSO at room temperature, and this precluded the use of DMSO for obtaining accurate spectra. However, DMF behaves as a relatively inert solvent for both complexes, the spectra remaining unchanged for at least 15 min after dissolution of the complex, so that accurate measurements were readily made. At room temperature the *trans* isomer is sufficiently stable in water at pH 6 for its spectrum to be

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(24) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, Inc., New York, Amsterdam, 1964, p 78 ff. The energy-level diagram given is actually for NO_2, but in considering O_3 and SO_2 the authors extend the discussion to 18 valence electron systems such as NO_2^-.

(25) B. M. Gatehouse, *J. Inorg. Nucl. Chem.*, **8**, 79 (1958).

(26) A. P. Altshuller, I. Cohen, and C. M. Schwab, *J. Phys. Chem.*, **62**, 621 (1958).

(27) Aromatic nitro compounds, especially polysubstituted ones, may show an absorption band in this region, not necessarily due to the nitro group. If the latter interacts strongly with the aromatic system, the $^1A_1 \rightarrow {}^1A_2$ (equivalent to $n_0 \rightarrow \pi^*$) transition may be shifted to much lower energies.

readily taken, but *cis*-$\mathrm{Cr(en)_2(ONO)_2^+}$ is rapidly aquated in water at pH 6. Hence, to obtain the aqueous spectrum of this ion, repeated scans at known short time intervals were made and the traces then extrapolated back to zero time. Figures 2 and 3 give the initial spectra of both geometrical isomers in DMF and aqueous solution. It can be seen that even in aqueous solution both complexes exhibit splitting and several weak shoulders on the maximum near 340–350 mμ. Since neither complex is of true O_h symmetry, however, some splitting of the octahedral Cr(III) bands is expected, and the aqueous spectra cannot therefore be taken as conclusive evidence of ligand absorption around 360 mμ. Fortunately, the sharp peaks in the DMF spectra leave little doubt of the presence of such absorption in both cases, unless it is assumed that the d–d bands in the relevant region show, in this solvent, the vibrational structure they theoretically contain. This possibility is strongly negated by: (1) the correspondence in both number and wavelengths of the sharp maxima with those in alkyl nitrites, nitrite ion, and nitrous acid; (2) the lack of any splitting in the first (low-energy) d–d band (*ca.* 480 mμ) of either complex; (3) the lack of any splitting in the second d–d band (near 360 mμ) of the corresponding $\mathrm{Cr(en)_2(OH_2)_2^{3+}}$ cations in DMF. That the absorption does not arise from free $\mathrm{NO_2^-}$ released by solvolysis is shown by the fact that the spectrum of sodium nitrite in DMF is much less well resolved (Figure 1).

Further substantiation of the belief that the sharp peaks in DMF and shoulders in water were due to nitrito ligands arose from the observation of similar absorption in the electronic spectra of $\mathrm{[Cr(NH_3)_5ONO](ClO_4)_2}$, $\mathrm{[Co(NH_3)_5ONO](ClO_4)_2}$, and *cis*-$\mathrm{[Co(NH_3)_4(ONO)_2]ClO_4}$, and its absence in the spectra of $\mathrm{[Co(NH_3)_5NO_2](ClO_4)_2}$, *cis*-$\mathrm{[Co(NH_3)_4(NO_2)_2]ClO_4}$, and *trans*-$\mathrm{[Co(en)_2(NO_2)_2]ClO_4}$. Only $\mathrm{[Cr(NH_3)_5ONO](ClO_4)_2}$ and *cis*-$\mathrm{[Co(NH_3)_4(ONO)_2]ClO_4}$ showed detectable splitting in water. The splitting in the Co(III) nitrito complexes is less marked than in the Cr(III) compounds, and this may be due to more intense overlapping absorption from other sources (*e.g.*, charge transfer). Similar relatively strong absorption may explain why Goodgame and Hitchman[2] did not observe any fine structure around 360 mμ in their spectra of several dinitritobis(diamine)nickel(II) complexes. In a later paper,[28] these same authors give spectra for some Co(II) and Ni(II) complexes containing bidentate nitrite, but since the spectra published do not extend below 400 mμ the presence or absence of such fine structure cannot be checked at this time. Assuming $\begin{matrix}-\mathrm{O}\\-\mathrm{O}\end{matrix}\!\!>\!\mathrm{N}$ chelation in their complexes, absorption by the complexed nitrite around 360 mμ would be expected, and its appearance should afford ready distinction from $^{-\mathrm{O}}\!\!>\!\mathrm{N{-}O}$ chelation.

The spectra of *cis*- and *trans*-$\mathrm{Cr(en)_2(ONO)_2^+}$ in DMF only give proof that at least one of the nitrite ligands is bonded nitrito and do not eliminate the possibility of nitrito–nitro coordination. There appears to be no such ambiguity with regard to the solid-state configuration, however. The diffuse reflectance spectra of both complexes as perchlorate salts (Figure 4) are very similar to those in DMF, and the fine structure around 360 mμ is well resolved. Since the solid-state infrared spectrum of neither complex shows any evidence of an $\mathrm{-NO_2}$ wagging mode absorption, this must mean that both have a dinitrito configuration in the solid state as perchlorate salts. Initially at least, this is as expected from the known mechanism of formation of nitrito complexes in acid medium.[23,29,30] Of great relevance to the determination of the solution configuration is the fact that the solid-state infrared spectra seem to be almost time invariant. The spectrum of *cis*-$\mathrm{[Cr(en)_2(ONO)_2]ClO_4}$ remains unchanged for at least 3 weeks after preparation, and that of the *trans* compound shows negligible changes over periods of 18 months or more (when kept in the dark).[31] These results suggest that any –ONO to $\mathrm{-NO_2}$ isomerization, if it occurs at all, must be extremely slow in either case. Comparison then with the known relative rates of solution and solid-state –ONO to $\mathrm{-NO_2}$ isomerizations in analogous systems[32] indicates that, for *cis*- and *trans*-$\mathrm{[Cr(en)_2(ONO)_2]ClO_4}$ nitrito ligand isomerization within the time of dissolution in either DMF or $\mathrm{H_2O}$ would not occur to any appreciable extent. Hence, the sharp peaks in DMF and multiple shoulders in water must arise from complexes with the dinitrito configuration. Other factors, such as the similarity of the solid-state and solution spectra and the intensity of absorption around 360 mμ, are consistent with this assignment.

The possibility of –ONO to $\mathrm{-NO_2}$ isomerization in solution is not negated by any of the above, of course. In the case of *cis*-$\mathrm{Cr(en)_2(ONO)_2^+}$ in water, the solvent of foremost interest, rapid aquation of the complex makes it impossible to decide on this point. With *trans*-$\mathrm{Cr(en)_2(ONO)_2^+}$, however, kinetic data so far accumulated on its reactions in aqueous solution[33] give no evidence at all of any ligand isomerization occurring. Studies[4,5,32] of $\mathrm{Cr(NH_3)_5ONO^{2+}}$ salts have shown that this complex also has no tendency to isomerize to $\mathrm{Cr(NH_3)_5NO_2^{2+}}$ in the solid state or in solution and suggest that, for some reason, Cr(III) will not form a stable bond to the nitrogen in $\mathrm{NO_2^-}$. (The reason may be, as stated initially, that Cr(III) is incapable of π donation to $\mathrm{-NO_2}$, steric factors also tending to favor –ONO; alternatively, Cr(III) may simply have a very large affinity for bonding to oxygen, as is suggested by

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[28] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **4**, 721 (1965).

[29] R. K. Murmann, *J. Am. Chem. Soc.*, **77**, 5190 (1955).

[30] R. K. Murmann and H. Taube, *ibid.*, **78**, 4886 (1956).

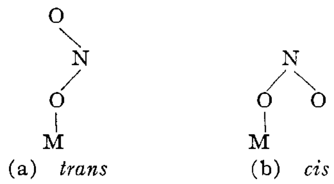
[31] The KCl disk infrared spectrum of the *trans* nitrate salt shows marked changes within 2 weeks of preparation. These do not seem to be consistent with any –ONO to $\mathrm{-NO_2}$ isomerization, however, being more suggestive of an oxidation–reduction reaction between the nitrate anion and one nitrito ligand, in which the nitrito ligand is converted to a nitrato ligand by oxygen atom transfer from a free nitrate anion, leaving it as a free nitrite anion. Whatever their source, the changes must be reversible, as the nitrate salt gives the same ultraviolet–visible spectrum in $\mathrm{H_2O}$ regardless of age of the solid.

[32] F. Basolo and G. S. Hammaker, *Inorg. Chem.*, **1**, 1 (1962).

[33] Work from these laboratories to be published later.

other evidence.) Thus, there is very little uncertainty in the formulation of the new complexes of this paper as *cis*- and *trans*-$Cr(en)_2(ONO)_2^+$ cations in both solution and the solid state.

Alkyl nitrites can exhibit *cis–trans* rotational isomerism, and these rotational isomers are quite different in regard to wavelengths and intensities of the vibrational structure in the 300–400-mμ band.[34] For the inorganic nitrito compounds discussed in this paper, the split peaks around 360 mμ correspond best to those found in *trans* alkyl nitrites; *i.e.*, it seems probable that the metal bonds to an oxygen atom at a position which puts it *trans* to the other oxygen atom, as shown in Figure 5 (a). This result is as expected simply on consideration of steric interaction with ethylenediamine ligands.



(a) *trans* (b) *cis*

Figure 5.—Possible rotational isomers for a group coordinated to the oxygen of nitrite ion.

In conclusion, a distinguishing criterion based on spectral differences of organic nitro compounds and alkyl nitrites seems valid in relation to inorganic nitro and nitrito complexes. Such differentiation by spectroscopic means is useful in inorganic systems where absorption by the metal group in the region 300–400 mμ is not strong.

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Substituent Exchange Equilibria between the Dimethyl- and Trimethylsilicon Moieties

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Scrambling equilibria resulting from the exchange of pairs of monofunctional substituents between the difunctional dimethylsilicon and the monofunctional trimethylsilicon moieties have been studied by proton nuclear magnetic resonance. The resulting data have been evaluated in terms of two equilibrium constants, one describing the scrambling of the two kinds of substituents on the dimethylsilicon moiety and another one, an intersystem constant, representing the distribution of the two kinds of monofunctional substituents between the dimethyl- and trimethylsilicon moieties. The observed deviations of the latter constant from the value for ideal random sorting have been attributed to π-bonding effects.

In previous papers[1-3] from this laboratory, quantitative data were reported regarding substituent-exchange equilibria in systems in which two different monofunctional substituents were scrambled between two kinds of central moieties, both exhibiting a given functionality of either 2 or 3. The present paper contains examples of exchange in systems of the above kind where the monofunctional substituents exchange between central moieties of different functionalities—in this case $(CH_3)_2Si<$ and $(CH_3)_3Si–$. The studies reported herein are related to two other communications[4,5] dealing with exchange equilibria in systems where the two monofunctional substituents exchange between $CH_3Si\lessdot$ and $(CH_3)_2Si<$ and between $CH_3Si\lessdot$ and $(CH_3)_3Si–$. In all of these investigations, the methylsilicon moieties remain intact and do not exchange methyl groups under the chosen reaction conditions.

Experimental Section

Materials.—Trimethylchlorosilane and dimethyldimethoxysilane were obtained from the Anderson Chemical Co., Weston, Mich., and fractionated before use. Trimethylbromosilane,[5] dimethylbis(methylthio)silane,[6] dimethyldibromosilane,[7] and dimethylbis(dimethylamino)silane[8] were prepared according to procedures of the literature.

Equilibration and Measurements.—Mixtures of the two components, $(CH_3)_2SiZ_2$ and $(CH_3)_3SiT$, in various mole ratios were sealed in 5-mm o.d. precision nuclear magnetic resonance (nmr) tubes and heated at 120°. Equilibrium was assumed to be attained when the nmr pattern of pilot samples did not exhibit further changes upon additional heating. The samples were

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(1) K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **5**, 547 (1966).

(2) J. R. Van Wazer, K. Moedritzer, and L. C. D. Groenweghe, *J. Organometal. Chem.* (Amsterdam), **5**, 420 (1966).

(3) K. Moedritzer and J. R. Van Wazer, *J. Inorg. Nucl. Chem.*, **28**, 957 (1966).

(4) K. Moedritzer and J. R. Van Wazer, *Z. Anorg. Allgem. Chem.*, **345**, 35 (1966).

(5) K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **5**, 1254 (1966).

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(8) H. Breederveld and H. I. Waterman, *Research* (London), **5**, 537 (1952).