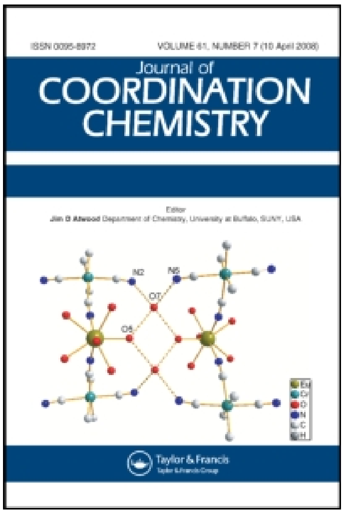

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# A REINVESTIGATION OF THE ACTION OF NITRIC OXIDE ON DIMETHYLZINC AND DIMETHYLCADMIUM

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# A REINVESTIGATION OF THE ACTION OF NITRIC OXIDE ON DIMETHYLZINC AND DIMETHYLCADMIUM[1]

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The reactions of the dimethylmetals, $Me_2M$ (M = Zn, Cd), with nitric oxide have been reinvestigated. Two moles of NO are taken up per mole of dimethylmetal in each case. Infrared, laser Raman and mass spectral data indicate that the $Me_2M.2NO$ adducts are best formulated as MeM[O.N(NO)Me] rather than $Me_2M.M[O.N(NO)Me]_2$ as had been suggested earlier. On hydrolysis, the methyl(N-methyl-N-nitrosohydroxylamine)metal(II) complexes apparently disproportionate to yield $M[O.N(NO)Me]_2$ and $M(OH)_2$.

## INTRODUCTION

While the reactions of transition metal compounds with nitric oxide have been widely studied,[2] similar reactions of non-transition metal compounds have received relatively little attention. In 1857, Frankland claimed[3] that the dialkylzinc compounds, $R_2Zn$ (R = Me, Et), reacted with NO to form products which he formulated as $R_2Zn.Zn[O.N(NO)R]_2$. Moreover, he also reported that these products gave $Zn[O.N(NO)R]_2$ on hydrolysis. No further research was carried out in this area until 1962 when Abraham *et al.*[4] reported briefly on their study of the analogous reactions of $Pr^n_2Zn$ and $Me_2Cd$ with NO. Their work revealed that two moles of NO were absorbed per mole of dialkylmetal and they proposed that the initial product in the case of $Pr^n_2Zn$ was $Pr^nZn[O.N(NO)Pr^n]$ rather than $Pr^n_2Zn.Zn[O.N(NO)Pr^n]_2$ as would have been expected on the basis of Frankland's earlier study. The subsequent hydrolysis product was formulated as $Zn[O.N(NO)Pr^n]_2$. Abraham *et al.* did not discuss the nature of the initial product in the $Me_2Cd$ reaction, but they considered the hydrolysis product to be $Cd[O.N(NO)Me]_2$. These authors mentioned that nmr data were supportive of the proposed structures, as was the absence of any $\nu$(NO) absorptions in the 2000–1500 $cm^{-1}$ region of the ir spectra of the zinc products. However, the complete details of their investigation have never been published.

As part of a broad study on the addition chemistry of the Group IIA organometals, we have now reinvestigated the reactions of $Me_2Zn$ and $Me_2Cd$ with NO and have used various spectroscopic techniques in order to establish the structures of the reaction products more definitively.

## EXPERIMENTAL

The chemicals were obtained from the sources indicated: $Me_2Zn$ and $Me_2Cd$ (Alfa Inorganics, Inc.), NO (Matheson of Canada, Ltd.), spectrograde cyclohexane (Fisher Scientific Co.).

Infrared and Raman spectra were recorded as described previously.[5] Mass spectra were obtained on an AEI Model MS902 spectrometer operating at 70 eV. Unless otherwise noted, elemental analyses were performed on a Hewlett-Packard Model 185 CHN Analyzer. Decomposition points were measured on a Gallenkamp melting point apparatus.

Since both $Me_2Zn$ and $Me_2Cd$ are volatile, toxic, air- and moisture-sensitive liquids, they had to be handled either by vacuum line techniques or under a dry, oxygen-free nitrogen atmosphere. All apparatus and solvents were purged repeatedly by vacuum/gaseous nitrogen cycles before use. The nitrogen gas was purified by passage first through a column of molecular sieves (Linde 5A), then through a column of heated copper turnings to remove any oxygen and finally through another column of molecular sieves.

For transfer of the dimethylmetals from the shipping ampoules to the storage vessels (which were fitted with Teflon "Rotaflo" valves), a well-purged, nitrogen-filled dry box (Fisher Vacutrol) was used.

### *Reactions of $Me_2Zn$ and $Me_2Cd$ with NO*

One typical reaction will be described in detail. The reaction vessel was a double Schlenk tube (DST) fitted with a fine, fritted glass disk for the purposes of filtration and product washing.

Cyclohexane (10 ml) was frozen (–196°) in the left leg of the DST and $Me_2Zn$ (0.125 ml, 1.82 mmole) was condensed onto the solid cyclohexane. The mixture was then warmed briefly to room temperature and quickly cooled to –78°. The vacuum line, Hg manometer[6] and tubing leading to the NO cylinder were evacuated and NO gas was admitted to the line. Then, NO gas (~4.6 mmole) was condensed at –196° into the left leg of the DST. After warming up to room temperature, the reaction mixture was stirred magnetically. Any excess NO gas remaining in the vacuum system was condensed out in a –196° trap. After 1 hr, the reaction mixture was cooled to –78° and the DST was opened to the vacuum line so that any condensables (e.g., unreacted NO) could be trapped out at –196°. The reaction mixture was again allowed to return to room temperature and the DST was disconnected from the vacuum line and transferred to a nitrogen-filled dry box. The DST was then tilted so that the reaction mixture was filtered from the left leg through the fritted glass disk into the right leg. The white precipitate which remained on the filter was washed with cyclohexane (7 ml). The filtrates were discarded and the DST was reconnected to the vacuum line and the precipitate was dried under vacuum (0.05 torr/25°). After drying, the precipitate was transferred to a dried sample vial and stored in a nitrogen-filled glove bag. The manometer measurements taken before and after the reaction indicated that 2.05 moles of NO were taken up per mole of $Me_2Zn$. *Anal.* (Daessle Microanalyses, Montreal, Quebec, Canada). Calcd for $C_2H_6N_2O_2Zn$: C, 15.5; H, 3.9; N, 18.0. Found: C, 15.6; H, 4.0; N, 18.7. Molecular weight: calcd, 154; found, 154 (mass spectrum). Yield: 0.212 g, 75%. The compound underwent hydrolysis when left overnight in a sealed desiccator containing a small dish of water.

The reaction of $Me_2Cd$ with NO was carried out under identical conditions to those described above. The manometer measurements indicated that 1.96 moles of NO were absorbed per mole of $Me_2Cd$. *Anal.* Calcd for $C_2H_6N_2O_2Cd$: C, 11.9; H, 2.3; N, 13.9. Found: C, 11.1; H, 2.8; N, 13.8. Molecular weight: calcd, 202; found, 202 (mass spectrum). Yield: 0.168 g, 59%. The compound also underwent hydrolysis when treated as described above. Analytical and mass spectral data (*vide infra*) suggested that the hydrolysis product was a 1:1 mixture of $Me_2Cd(NO)_4$ and $Cd(OH)_2$. *Anal.* Calcd for $C_2H_8N_4O_6Cd_2$: C, 5.9; H, 2.0; N, 13.7. Found for samples from two different preparations: C, 6.0, 5.6; H, 1.8, 2.0; N, 13.9, 13.6. Molecular weight: calcd for $C_2H_6N_4O_4Cd$, 262; found, 262 (mass spectrum).

Both the initial and hydrolyzed products are fine, white powders which do not melt sharply but decompose gradually to gold-coloured materials (>100° for the initial zinc product, >130° for the initial cadmium product and >200° for the hydrolyzed products). When freshly prepared, the initial products dissolve in dry, oxygen-free benzene, but not to concentrations sufficient to obtain nmr spectra. Moreover, soon after dissolution, fine, white precipitates (presumably decomposition products) appear. The materials obtained on hydrolysis of the initial products are insoluble in water and all common organic solvents.

## RESULTS AND DISCUSSION

### *Characterization of the Products Formed in the Reactions of $Me_2M$ (Me = Zn, Cd) with NO*

*1. Initial products* Both $Me_2Zn$ and $Me_2Cd$ readily absorb two moles of NO per mole of dialkylmetal on reaction with NO and the analytical and mass spectral data for the initial products are consistent with the formation of the 1:2 adducts, $Me_2M.2NO$. This means that Frankland's formulation[3] of the initial product in the $Me_2Zn$ reaction as $Me_2Zn.Zn[O.N(NO)Me]_2$ must be wrong, although he did have the correct $Me_2Zn$:NO ratio. In their work on the reaction of $Me_2Cd$ with NO, Abraham *et al.*[4] did not discuss the stoichiometry of the initial product formed. However, on the basis of their investigation of the reactions of several organometallic compounds with NO, they formulated the initial product in the case of $Pr^n_2Zn$ as $Pr^nZn[O.N(NO)Pr^n]$, i.e., $Pr^n_2Zn.2NO$.

The major fragments observed in the mass spectra of the $Me_2M.2NO$ adducts are listed in Table I. Since both zinc and cadmium poses several stable isotopes, the metal-containing fragments are readily identified. The parent molecular ions are observed for both com-

TABLE I.
Principal fragments in the mass spectra of the initial and hydrolyzed products of the reactions of $Me_2M$ (M = Zn, Cd) with NO[a]

| Initial Products | | | | Hydrolyzed Products | | | | |
|---|---|---|---|---|---|---|---|---|
| $^{64}$Zn Compound | | $^{112}$Cd Compound | | $^{64}$Zn Compound | | $^{112}$Cd Compound | | |
| m/e | Rel. Abund. | m/e | Rel. Abund. | m/e | Rel. Abund. | m/e | Rel. Abund. | Proposed Positive Ion Fragments |
| | | | | 214 | vw | 262 | vw | $(CH_3)_2M(NO)_4^+$ |
| | | 239 | vw | | | | | $CH_3M_2^+$ |
| | | | | 184 | 100 | 232 | 70 | $(CH_3)M(NO)_3^+$ |
| 203 | vw | | | | | | | $CH_3M_2^2(NO)_2^+$ |
| 154 | 0.1 | 202 | vw | 154 | vw | 202 | vw | $(CH_3)_2M(NO)_2^+$ |
| 139 | 0.2 | 187 | vw | 139 | 80 | 187 | 50 | $CH_3M(NO)_2^+$ |
| 124 | 44 | 172 | 0.5 | 124 | 40 | 172 | 5 | $M(NO)_2^+$ |
| 109 | 0.3 | 157 | 0.1 | 109 | 60 | 157 | 50 | $CH_3M(NO)^+$ |
| 108 | 0.1 | | | | | | | $CH_2M(NO)^+$ |
| 94 | 12 | 142 | 38 | 94 | 10 | 142 | 30 | $M(NO)^+$ |
| 79 | 100 | 127 | 100 | 79 | 50 | 127 | 50 | $CH_3M^+$ |
| 64 | 16 | 112 | 59 | 64 | 30 | 112 | 100 | $M^+$ |

[a] The spectra were all recorded at ~150°. The intensity of the strongest peak in each spectrum has been arbitrarily set to 100.

pounds, but with extremely low intensities. The base peak in both cases is the $CH_3M^+$ fragment strongly suggesting that at least one methyl group is coordinated to the metals in the parent molecules. The peaks at *m/e* P–15 and P–45 can best be attributed, therefore, to $CH_3M(NO)_2^+$ and $CH_3M(NO)^+$, respectively. This in turn suggests that at least one nitrosyl group must be bonded directly to the metals. There are also a series of low intensity, high molecular weight fragments appearing in both spectra which we attribute to metal-metal bonded species (e.g., $Cd{-}CdCH_3^+$) formed by rearrangements occurring within the mass spectrometer. On the basis of the mass spectral evidence, therefore, it seems reasonable to formulate the $Me_2M.2NO$ adducts as $MeM(NO)_2Me$, where the nature of the bonding in the $M(NO)_2Me$ moiety remains to be established.

The ir and Raman spectra of the two adducts (Table II) are very similar with most of the peaks in the spectra of the cadmium product occurring at slightly lower energies than those of the zinc compound. Many of the bands appear in both the ir and the Raman with approximately the same relative intensities.

In the C–H stretching region, there are bands attributable to both $M{-}CH_3$ and $N{-}CH_3$ vibrations. The former are close in frequency and relative intensity to those for the liquid dimethylmetals.[7] There are no bands in the 2000–1500 $cm^{-1}$ region characteristic of coordinated terminal nitrosyl groups,[2] but the bands at ~1385 $cm^{-1}$ can be assigned to $\nu(N{=}O)$ vibrations by comparison with the spectra of nitrosoamines ($R_2{-}N{-}N{=}O$).[8] In addition, we have attributed the strong bands in the spectra of the adducts at ~1065 $cm^{-1}$ to $\nu(N{-}N)$ because those of nitrosoamines[8] and the hyponitrite ion $[(O{-}N{-}N{-}O)^{2-}]$[9] fall in the 1110–1050 $cm^{-1}$ range. In the Raman, the $\nu(M{-}C)$ modes of organometallic compounds are usually the most intense bands observed in the low frequency region.[7,10] Consequently, we have attributed the very strong Raman bands at 546 (Zn product) and 480 $cm^{-1}$ (Cd product) to $\nu(M{-}C)$ vibrations. That there is only one $\nu(M{-}C)$ band for each compound suggests that there is only one methyl group bonded directly to the metals because from our work on the $Me_2M.L{-}L$ adducts of the dimethylmetals with bidentate ligands (L–L),[11] two very strong Raman-active $\nu(M{-}C)$ bands are always observed.

The vibrational data together with the mass spectral evidence discussed earlier indicate that the $Me_2M.2NO$ adducts can best be formulated as MeM[O.N(NO)Me] (I), i.e., similar to the $Pr^nZn[O.N(NO)Pr^n]$ formula proposed by Abraham *et al.*[4] for the initial product in the reaction of $Pr_2^nZn$ with NO. All the vibrational assignments given in Table II, therefore, are based on the MeM[O.N(NO)Me] formulation and have been made by comparison with the spectra of nitrosoamines[8] and the tetrameric $(MeMOMe)_4$ species.[12]

In their communication, Abraham *et al.*[4] suggested that $Pr^nZn[O.N(NO)Pr^n]$ was formed by a mech-

TABLE II.

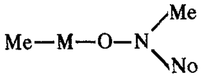
Vibrational spectra (cm$^{-1}$) of the initial and hydrolyzed products of the reactions of Me$_2$M (M = Zn, Cd) with NO

| Initial Products | | | | Hydrolyzed Products | | | | |
|---|---|---|---|---|---|---|---|---|
| Zinc compd. | | Cadmium compd. | | Zinc compd. | | Cadmium compd. | | Proposed vibrational assignments |
| Infrared[a] | Raman[b] | Infrared[a] | Raman[b] | Infrared[a] | Raman[b] | Infrared[a] | Raman[b] | |
| | | | | | | 3400 vs | | ν(O–H) [Cd(OH)$_2$] |
| 3045 m | 3044 m | 3037 vw | 3040 m | | 3041 m | | 3052 w | ν(C–H) (N–CH$_3$) |
| | 3026 w | | | | 3027 m | | 3020 s | |
| | 3012 w | 3010 vw | 3012 w | | | | 3001 m | |
| 2954 s | 2962 s<br>2951 m<br>2942 s | 2960 s | 2957 vs | | | | | ν(C–H) (M–CH$_3$) |
| 2912 m | 2913 s | 2913 s | 2912 vs | | | | | |
| | | 2882 vw | | | 2962 vs | | 2960 s<br>2932 m | |
| 2847 m | 2849 m,br | 2842 m | 2848 w<br>2841 sh | | 2815 vw | | 2820 w | 2 x δ(CH$_3$)(~1430) |
| 1477 m | 1481 w | 1463 m | 1467 w | 1469 w | | | 1473 vw, br | δ(CH$_3$) |
| 1431 m | 1430 w | 1427 m | 1426 w | | 1428 w,sh | 1440 w,br | 1443 w | |
| 1414 s | 1415 s | 1405 s | 1405 s | 1415 m | 1414 m | 1415 m | 1403 m | |
| 1392 s | 1387 s | 1383 m | 1378 s | 1375 s | 1380 s,br | 1359 s | 1377 vs<br>1362 w,sh | ν(N=O) |
| 1296 s,br | 1300 m ,br | 1293 s,br | 1294 m | 1300 s | 1306 s | 1281 s | 1286 s | |
| 1267 s<br>1243 s | | 1212 s<br>1190 s | 1190 m | 1233 s | 1219 w | 1240 s | 1230 m | δ(N–CH$_3$) |
| 1150 w | 1172 w<br>1159 vs<br>1155 w,sh | 1131 w | 1153 w<br>1128 vs | | | | | δ(M–CH$_3$) |
| 1118 w | | 1114 w | | | 1133 vw | | | |
| 1064 s | 1070 s | 1058 m | 1061 s | 1068 m | 1071 m<br>1062 m | 1058 w | 1066 s<br>1056 s | ν(N–N) |
| 970 s | 976 m | 954 s | 966 m | 993 m<br>958 s<br>938 s | 952 m | 958 m,br<br>935 s | 950 s<br>940 m | ν(C–N) |
| 956 s | 969 s | 938 sh | 955 m | | | 921 s | | ν(O–NO) |
| | | | | 838 m | | 849 m | | |
| 707 s | 713 m | 710 m | 710 m | 704 s | 711 s | 702 m<br>692 s | 712 m<br>695 m | δ(N–N=O) |
| 679 w,sh<br>664 m,br | 669 vw,br | 672 sh<br>651 s,br | 655 vw | | | | | (M–CH$_3$)rock |
| 590 w, sh | 594 w | | | | | | | |
| 581 m | | | | | | | | |
| 576 w,sh | 568 w | 558 w<br>545 m | 543 w<br>533 w | 567 s | 564 w,sh | 567 w | 564 w,br | |
| 542 m | 546 vs | 478 m | 480 vs | | | | | ν(M–C) |
| | 540 w,sh | | | | | | | |
| | | | | 553 m | 553 s | | 512 s | |
| | | | | | | 495 w | 501 w | |
| 430 w | 443 w | 416 w | 429 w | 447 w | 427 vw | 433 w | | |
| | | | | | 378 vw | 399 w | | |
| | 305 m | | 301 w | | | | 293 w | |
| | | | | | | | 271 w | |
| | 273 s | | 232 m | | 270 s | | 228 w | ν(M–O) |
| | 244 m | | | | | | | |
| | | | | | 226 m | | | |
| | | | 218 m | | | | | |
| | 155 w | | 104 s,br | | 140 m | | 190 m | δ(C–M–O), δ(O–M–O) and lattice modes |
| | 124 w | | 80 s | | 107 m | | 170 m | |
| | 89 s,br | | 66 s | | 77 w,sh | | 136 w | |
| | 65 w | | 54 m | | 64 s | | 103 vw | |
| | 56 w | | 43 w | | | | 86 s | |
| | 51 w | | | | | | 65 s | |
| | 42 s | | | | | | 54 s | |
| | 34 m | | | | | | 40 s | |
| | 29 w | | | | | | | |

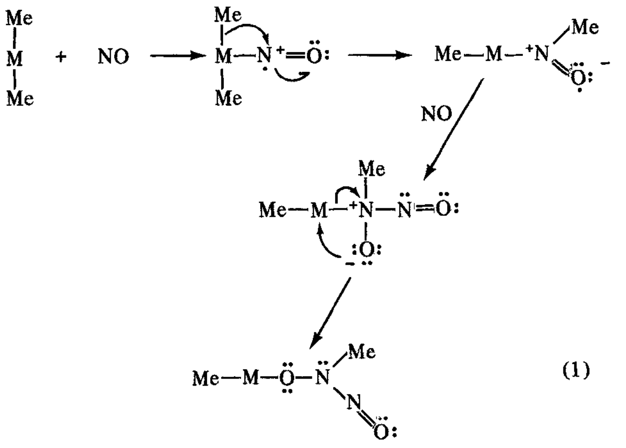
[a] In hexachlorobutadiene mull (4000–1350 cm$^{-1}$ region) and Nujol mull (1350–400 cm$^{-1}$ region).

[b] For powdered solid in capillary tube at room temperature using 514.5 nm Ar$^+$ laser excitation. Note that the observed frequencies have been divided into three sections and the intensities given are relative to the strongest peak within each section.

anism involving initially O-coordination of one NO molecule to $Pr^n_2Zn$, followed by a 1,3-shift of a methyl group and attachment of the second NO molecule to the N atom of the first one. However, in view of the known preference of N-coordination of NO molecules to metals,[2] we favour the mechanism shown in eq. 1 for the formation of the methyl(N-methyl-N-nitrosohydroxylamine)metal(II) complexes.



(I) M = Zn, Cd



(1)

2. *Hydrolysis products* Both the zinc and cadmium products formed on hydrolysis of the MeM[O.N(NO)Me] compounds exhibit similar fragmentation patterns in their mass spectra (Table I). The highest molecular weight, metal-containing ions correspond to the $Me_2M(NO)_4^+$ species. The mass spectra show peaks due to the loss of $CH_3$ and NO groups and the fragmentation patterns are consistent with $M[O.N(NO)Me]_2$ formulae proposed earlier by Frankland[3] and Abraham *et al.*[4] Analytical data for the freshly prepared cadmium product agree with the $HOCd[O.N(NO)Me]_2$ formulation rather than $Cd[O.N(NO)Me]_2$. However, it occurred to us that $HOCd[O.N(NO)Me]_2$ has the same stoichiometry as a 1:1 mixture of $Cd[O.N(NO)Me]_2$ and $Cd(OH)_2$ and we believe that the initial MeM[O.N(NO)Me] products disproportionate upon hydrolysis according to eq. 2.

$$2MeM[O.N(NO)Me] + H_2O \longrightarrow M[O.N(NO)Me]_2 + M(OH)_2 \qquad (2)$$

All our efforts to separate the two cadmium products were unsuccessful. The $M[O.N(NO)Me]_2$ compounds do not sublime and are insoluble in water and all common organic solvents thus precluding any nmr measurements. The comment concerning nmr data in the preliminary communication of Abraham *et al.*[4] presumably referred to the $Pr^n_2Zn$ products rather than the $Me_2Cd$ ones.

Infrared and Raman data for the two hydrolyzed products are given in Table II. As expected in view of the similar groupings involved, the spectra are quite similar to those of the initial products. Again, there is no evidence of coordinated nitrosyl groups, but bands due to $\nu(N{=}O)$ and $\nu(N{-}N)$ are clearly discernible. Moreover, as expected, the intense Raman bands attributed to the $\nu(M{-}C)$ modes in the spectra of the initial products are completely absent in the spectra of the hydrolysis products.

## CONCLUSIONS

This study has verified that the initial products in the reactions of $Me_2M$ (M=Zn, Cd) with NO have the formula, $MeM[O.N(NO)Me]_2$. There is no evidence of terminal nitrosyl groups being bonded directly to the metals. Analytical, vibrational and mass spectral data suggest that the MeM[O.N(NO)Me] species hydrolyse to form $M[O.N(NO)Me]_2$ and $M(OH)_2$.

## ACKNOWLEDGMENTS

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## REFERENCES

1. Taken in part from the M.Sc. thesis of M.L.N., McGill University, Montreal, Quebec, Canada, 1974.
2. For example, see W. P. Griffith, *Adv. Organometal. Chem.*, 7, 211 (1968).
3. E. Frankland, *Phil. Trans.*, **147**, 63 (1857).
4. M. H. Abraham, J. H. N. Garland, J. A. Hill and L. F. Larkworthy, *Chem. and Ind.*, 1615 (1962).
5. I. S. Butler and C. F. Shaw III, *J. Raman Spectrosc.*, 3, 65 (1975).
6. Since both $Me_2Zn$ and $Me_2Cd$ undergo metal exchange with elemental mercury, the Hg manometer was never exposed to the liquid dimethylmetals and traces of the compounds were never pumped through the Hg diffusion pump.
7. J. L. Durig and S. C. Brown, *J. Mol. Spectrosc.*, **45**, 338 (1973) and reference cited therein.
8. L. J. Bellamy, "The Infrared Spectra of Complex Mole-

cules", 2nd ed., Methuen and Co., London, 1958, Chapter 17.

9. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed., Wiley Interscience, New York, 1970, p. 104.
10. D. M. Adams and A. Squire, *J. Chem. Soc. A*, 814 (1970).
11. I. S. Butler and M. L. Newbury, to be published.
12. G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1870 (1965).