TETRAHEDRAL COMPLEXES FROM N,N' ETHYLENEDIMORPHOLINE[1]

ANTONE L. LOTT, II and PAUL G. RASMUSSEN

Department of Chemistry, University of Michigan, Ann Arbor, Mich. 48104

Abstract — The ligand N,N' ethylenedimorpholine (EDM) reacts with divalent first row transition metal halides to give complexes of the type $MX_2(EDM)$; (M = Zn, Cu, Co, Ni) (X = Cl, Br, I). Although there are four potential donor atoms in the ligand, two nitrogens and two oxygens, the ligand is bound through the two nitrogens thus behaving like a substituted ethylenediamine. The complexes, with the exception of the $NiBr_2$, NiI_2 and CoI_2 constitute in isomorphous series to which a distorted tetrahedral coordination geometry has been assigned, on the basis of their stoichiometry, their physical, magnetic, and spectral properties. The exclusive formation of distorted tetrahedral complexes is discussed in terms of the steric requirements of the ligand.

INTRODUCTION

MANY complexes of N-substituted ethylenediamines have been prepared and studied. The geometry of the complexes covers the range from octahedral to tetrahedral to square planar[2–5]. A ligand which can be viewed as a N-substituted ethylenediamine is N,N', ethylenedimorpholine (EDM) Fig. 1.
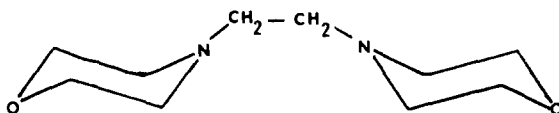
Fig. 1. Structure of N,N'-ethylenedimorpholine (EDM).

No systematic investigation of the ability of this ligand to form complexes with di-positive first row transition metal halides has been undertaken. EDM has been used in the past as a selective reagent in the gravimetric analysis of Hg^{2+}[6], Bi^{3+}[7], $PO_4{}^{3-}$[8], and Zn^{2+}[9]. The ligand has also been shown to form a complex with Ga(I) with the stoichiometry $[Ga(EDM)][GaX_4]$ (X = Cl–, Br–)[10]. In this complex the EDM presumably acts as a tetradentate ligand.

1. Presented in part at the 155th National meeting of the American Chemical Society, San Francisco, California, April 1–5 1968.
2. D. M. L. Goodgame and L. M. Venanzi, *J. chem. Soc.* 616, 5909 (1963).
3. L. Sacconi, I. Bertini and F. Mani, *Inorg. Chem.* 6, 262(1967).
4. I. Bertini and F. Mani, *Inorg. Chem.* 6, 2032 (1967).
5. S. F. Pavkovic and D. W. Meek, *Inorg. Chem.* 4, 20 (1965).
6. E. Asmus and K. Ohls, *Z. Analyt. Chem.* 177, 100 (1960).
7. E. Asmus, H. Haehne and K. Olds, *Z. Analyt. Chem.* 196, 161 (1963).
8. E. Asmus and J. Sarfert, *Z. Analyt. Chem.* 198, 412 (1963).
9. E. Asmus and J. Peters, *Z. Analyt. Chem.* 203, 409 (1964).
10. S. M. Ali, F. Brewer, J. Chadwick and G. Groton *J. inorg. nucl. Chem.* 9, 124 (1959).

These complexes all contain only one ligand per metal atom. There are four potential donor atoms in the ligand. Since molecular models indicated that all four atoms could achieve the proper spatial configuration for coordination, the present investigation was undertaken to determine what mode of coordination is actually utilized.

It is possible to detect oxygen coordination by shifts in the C–O–C i.r. stretching frequencies at 920 and 1065 cm^{-1}. Although the number of complexes where ethereal oxygen is coordinated is not large, a few have been reported in the literature[11–14].

We have found that in non-coordinating solvents zinc(II) chloride, copper(II) chloride and bromide, nickel(II) and cobalt(II) chlorides, bromides and iodides react with EDM to give complexes of the general formula $M(EDM)X_2$. The stereochemistry and the properties of these complexes have been studied and the results are reported in this paper.

EXPERIMENTAL

Materials. N,N'. ethylenedimorpholine was obtained from the Aldrich Chemical Co., with a stated purity of 98 per cent and was used without further purification[15]. The metal halides and all solvents were analytical grade except for 2,2', dimethoxypropane which was Eastman yellow label.

Preparation of the complexes. The complexes were prepared in two different ways depending on the metal ion involved. Anhydrous metal halides were either purchased from Alfa Inorganics Inc. or were prepared by heating the hydrated metal chloride in a drying oven at 150°C. for 10 hr.

(1) $CoCl_2$, $CoBr_2$, CoI_2, $CuCl_2$, $CuBr_2$, NiI_2

The anhydrous metal halide, 5 m-moles, was dissolved in 100 ml of absolute ethanol (boiling in the case of NiI_2) and 5 m-moles of the ligand dissolved in 50 ml of absolute ethanol were added to the solution of the metal halide with rapid stirring. The complexes precipitated from solution almost immediately. Stirring was continued for 20 min to insure completeness of reaction. The product was filtered and washed with 5×40 ml portions of anhydrous ether. The cobalt and nickel complexes were purified by Soxhlet extraction with methylene chloride. The copper complexes were not purified because of some decomposition during the time required for purification in all solvents utilized. However, satisfactory analytical data was obtained. Yields: cobalt complexes, 50–60%; copper complexes, 90–95%; Ni(EDM)I_2, 30–35%.

Anal. Calcd. for Co(EDM)Cl_2: C, 36·36; H, 6·09; Cl, 21·48. Found: C, 36·07; H, 6·03; Cl, 21·50. Calcd. for Co(EDM)Br_2: C, 28·66; H, 4·81. Found: C, 28·47; H, 4·78. Calcd. for Co(EDM)I_2: C, 23·41; H, 3·91. Found: C, 23·51; H, 3·94. Calcd. for Cu(EDM)Cl_2: C, 35·88; H, 6·02. Found: C, 35·45; H, 6·00. Calcd. for Cu(EDM)Br_2: C, 28·35; H, 4·76. Found: C, 28·39; H, 4·68. Calcd. for Ni(EDM)I_2: C, 23·42; H, 3·93. Found: C, 23·47; H. 3·89.

(2) $NiCl_2$, $NiBr_2$, $ZnCl_2$

A diffirent method of preparation had to be found for these complexes due to the difficulty in obtaining anhydrous $ZnCl_2$ and due to the low solubility and incompleteness of reaction of $NiCl_2$ and $NiBr_2$ in absolute ethanol. In a typical preparation 5 m-moles of the hydrated metal chloride were stirred in a 250 ml ground glass stoppered erlenmeyer flask with 100 ml 2,2 dimethoxypropane for 6 hr to insure complete dehydration of the metal chloride[16, 17]. EDM, 5 m-moles, dissolved in 50 ml of 2,2 di-

11. R. J. Kern, *J. inorg. nucl. Chem.* **24**, 1105 (1962).
12. M. D. Joesten, K. Claus and K. Lannert, *J. inorg. nucl. Chem.* **29**, 1421 (1967).
13. C. J. Pedersen, (a) *J. Am. chem. Soc.* **89**, 2495 (1967).
                    (b) *J. Am. chem. Soc.* **89**, 7017 (1967).
14. A. C. L. Su and J. F. Wieher, *Inorg. Chem.* **7**, 176 (1968).
15. M.P. as obtained 74°C. (listed, 73–74°C). After 2 recrystalizations from absolute ethanol m.p., 74°C.
16. K. Stark, *J. inorg. nucl. Chem.* **11**, 77 (1959).
17. J. T. Donoghue and R. S. Drago, *Inorg. Chem.* **1**, 866 (1962).

methoxypropane were added with rapid stirring. The time required for complex formation depends greatly on the metal halide. With $ZnCl_2$ the reaction is essentially complete within a minute while $NiCl_2$ requires an hour for complete reaction. $NiBr_2$ requires 36 hr. The complexes were filtered and washed with 5×40 ml portions of anhydrous ether. They were purified by Soxhlet extraction with methylene chloride. Yields: $NiCl_2$ and $NiBr_2$, 35–45%; Zn 50–60%.

Anal. Calcd. for $Ni(EDM)Cl_2$: C, 36·40; H, 6·09. Found: C, 36·22; H, 6·02. Calcd. for $Ni(EDM)Br_2$: C, 28·68; H, 4·81. Found: C, 28·78; H, 4·91. Calcd. for $Zn(EDM)Cl_2$: C, 35·68; H, 5·79. Found: C, 35·66; H, 5·85.

Physical measurements. I.R. spectra were recorded in the range 4000–625 cm^{-1} on a Perkin-Elmer Model 237 spectrophotometer as nujol mulls on NaCl plates. Near i.r., visible and u.v. spectra were recorded in the range 43,000–4000 cm^{-1} on a Cary Model 14 spectrophotometer with 1 cm matched quartz cells in methylene chloride or chloroform. Magnetic susceptibilities were measured by the Guoy method at room temperature, and by the NMR method at ambient temperatures[18]. E.S.R. experiments were performed on a Varian Associates Inc. V-4502 X-band spectrometer.

Elemental analyses for carbon and hydrogen were determined by Spang Microanalytical Laboratory, Ann Arbor, Michigan. Chloride analyses on the cobalt complex were done by gravimetric methods.

RESULTS

All of the complexes gave virtually identical i.r. spectra. Within the accuracy of the instrument (± 2 cm^{-1}) both of the C–O–C stretching frequencies (at 1065 and 920 cm^{-1}) are unchanged. X-ray powder patterns show that all the chloride complexes as well as the cobalt and copper bromides are isomorphous. The cobalt and nickel iodides and the nickel bromide are different from each other and also different from the chlorides.

A three dimensional X-ray structure analysis has been completed on the $CoCl_2EDM$ complex[19]. The complex exists as discrete monomeric units of $CoCl_2EDM$. The geometry about the cobalt atom is distorted tetrahedral array of two nitrogens and two chlorines. The closest Co–O approach is 4·14 Å. The co-ordination geometry of the three complexes that aren't isomorphous is inferred to be the same as that of the $Co(EDM)Cl_2$ complex from the similarity of physical properties.

Zinc. The white diamagnetic complex is stable in non-coordinating solvents such as chloroform and methylene chloride. Its solution spectra in methylene chloride exhibits no absorptions in the range 4000–43,000 cm^{-1}. It has been used as a host lattice to grow doped single crystals for E.S.R. and optical studies.

Copper(II) halides. The yellow (Cl) and brick red (Br) complexes are stable in dry chloroform and methylene chloride. In the solid state the chloride complex is not very stable. It decomposes slowly turning green in two to three weeks.

The solution spectra of the two complexes are very similar (See Fig. 2). The spectra are not easy to interpret. Other than intense change transfer bands at 26,000 cm^{-1} both complexes exhibit a broad adsorption from 4000–16,000 cm^{-1}. Within this band one is able to distinguish two maxima at 7700 cm^{-1} and 10,500 cm^{-1} for the chloride complex and 8200 cm^{-1} and 10,100 cm^{-1} for the bromide complex. In C_{2v} symmetry four transitions would be expected[20]. The other two are buried in this broad absorption envelop and therefore no realistic assignments can be made for the two bands that are observed.

18. D. F. Evans, *J. chem. Soc.* 2003 (1959).
19. W. R. Scheidt, Ph.D. thesis, University of Michigan, Ann Arbor, Michigan (1968).
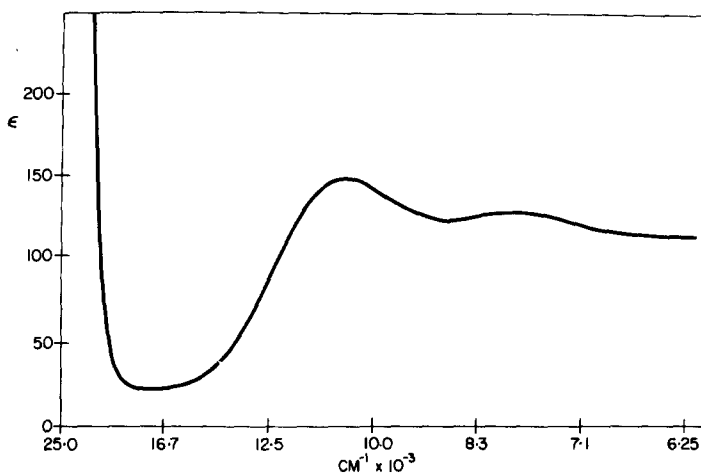20. G. Basee, R. Belford and R. Dickerson, *Inorg. Chem.* 1, 438 (1962).

Fig. 2. Eelectronic spectrum of Cu(EDM)Cl$_2$ in chloroform.

The room temperature magnetic moments for the Cu(II) complexes are 2·13 ± 0·03 B.M. for the chloride complex and 2·06 ± 0·04 B.M. for the bromide complex. These values though higher than most copper complexes are nevertheless consistent with the coordination geometry [4, 21].

Cobalt(II) halides. The chloride and bromide complexes are bright blue while the iodide is blue-green. They are soluble in chloroform and methylene chloride.

The solution spectra are all quite similar (see Fig. 3). The spectrophotometric data are presented in Table 1. In accordance with the assignments made by other authors [22, 23] the two bands between 6000 and 10,000 cm^{-1} are assigned to the
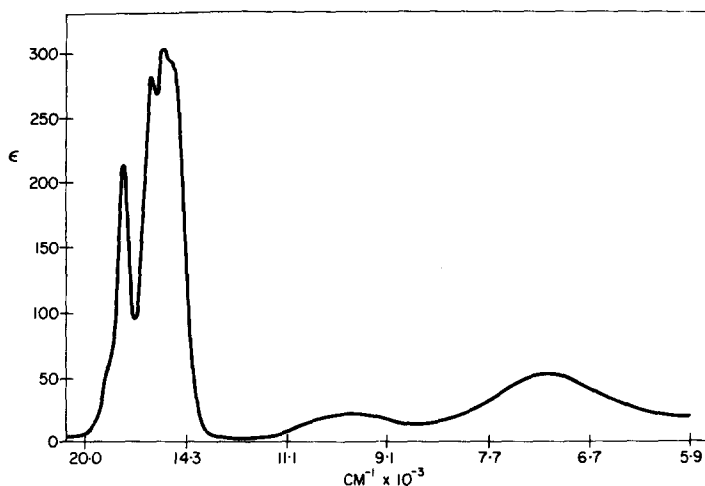

Fig. 3. Electronic spectrum of Co(EDM)Cl$_2$ in chloroform.

21. B. N. Figgis and C. M. Harris, *J. chem. Soc.* 855 (1959).
22. B. N. Figgis, *Introduction to Ligand Field Theory*, p. 234. Interscience, New York (1966).
23. D. L. Wood and J. P. Remeika, *J. chem. Phys.* **46**, 3595 (1967).

Table 1. Spectroscopic data for Cu(II), Ni(II) and Co(II) EDM complexes

Complexes	Solvent	Absorption max $(cm^{-1})(\epsilon_M)$
Cu(EDM)Cl$_2$	CHCl$_3$	7,700 (120), 10,500 (150).
Cu(EDM)Br$_2$	CH$_2$Cl$_2$	8,200 (200), 10,100 (250).
Ni(EDM)Cl$_2$	CHCl$_3$	9,340 (48), 11,350$_{sh}$ (16), 11,820 (13), 18,000 (93) 19,400 (84).
Ni(EDM)Br$_2$	CH$_2$Cl$_2$	9,625 (84), 10,925 (34), 11,300 (24), 17,325 (156), 18,175 (172).
Ni(EDM)I$_2$	CH$_2$Cl$_2$	9,175 (124), 10,150 (81), 16,550 (350).
Co(EDM)Cl$_2$	CHCl$_3$	7,050 (53), 9,800 (16), 14,600 (320), 15,070 (311), 15,700 (290), 17,250 (232), 18,200$_{sh}$ (70),
Co(EDM)Br$_2$	CH$_2$Cl$_2$	6,670 (65), 9,225 (47), 14,800 (542), 16,550 (292), 17,550$_{sh}$ (92).
Co(EDM)I$_2$	CH$_2$Cl$_2$	6,360 (97), 8,700 (69), 14,080 (742), 14,700 (742), 15,600 (432).

components of $^4A_2(F) \rightarrow {}^4T_1(F)$ (ν_2) transition in T_d symmetry and the bands between 14,000 and 20,000 cm^{-1} are assigned to the components of the $^4A_2(F) \rightarrow {}^4T_2(P)$ (ν_3) transition. The large splitting of these bands arises from distortions from true tetrahedral symmetry. The magnetic moments for the three complexes are normal for Co(II) in a distorted tetrahedral environment. They range from 4·48 B.M. for the chloride complex to 4·58 for the bromide to 4·60 for the iodide.

Although the iodide complex is not isomorphous with the chloride and bromide, whose structure is known, the similarity of the physical properties for the three complexes leads us to assign a distorted tetrahedral geometry to the iodide complex as well.

No E.S.R. signal was observed at 15,77,108, or 293°K and magnetic field strengths from 0 to 5,500 gauss for dilute single crystals of 1% CoCl$_2$(EDM) doped into ZnCl$_2$(EDM). With a $^4A_2$ ground state a signal should be readily obtainable if the sign of D (zero field splitting) is positive. In this case the ±1/2 state will lie lowest and the −1/2 → +1/2 transition should always be observable. On the other hand, if the sign D is negative the ±3/2 state will lie lowest with the ±1/2 state higher. If the magnitude of D is large then the ±1/2 states will not be populated at low temperatures and no signal will be observed. At higher temperatures, although the ±1/2 states will be populated, thermal relaxation will be rapid and a population difference will not be obtained; again leading to the absence of a signal. It has been found that in Cs$_3$CoCl$_5$ and Cs$_3$CoBr$_5$ the sign of D is negative and that its magnitude is large[24]. Thus we tentatively conclude from the absence of an E.S.R. signal that D is negative and its magnitude is large.

Nickel halides. The chloride and bromide complexes are purple while the

24. J. Owen, unpublished, quoted in K. D. Bower and J. Owen *Rep. Prog. Phys.* **22**, 204 (1959).

iodide is dark green. They are soluble in chloroform and methylene chloride. The bromide and iodide decompose in the solid state as well as in solution within a short time.

The solution spectra are similar with minor variations in band shapes and intensities (see Fig. 4). The band between 8000 and 10,000 cm^{-1} is assigned to the $^3T_1(F) \rightarrow {}^3A_2(F)$ (ν_2) transition and the bands between 16,000 and 20,000 cm^{-1} to the $^3T_1(F) \rightarrow {}^3T_1(P)$ (ν_3) transition of T_d symmetry. The two weak bands that appear on the short wavelength side of ν_2 are assigned to a spin forbidden transition to an upper state arising from the ^1D state of the free ion[25]. The intensities of these spin forbidden bands is abnormally large. This has been explained[26] by assuming that the ^1D state mixes with the nearby $^3A_2(F)$ via spin-orbit coupling.
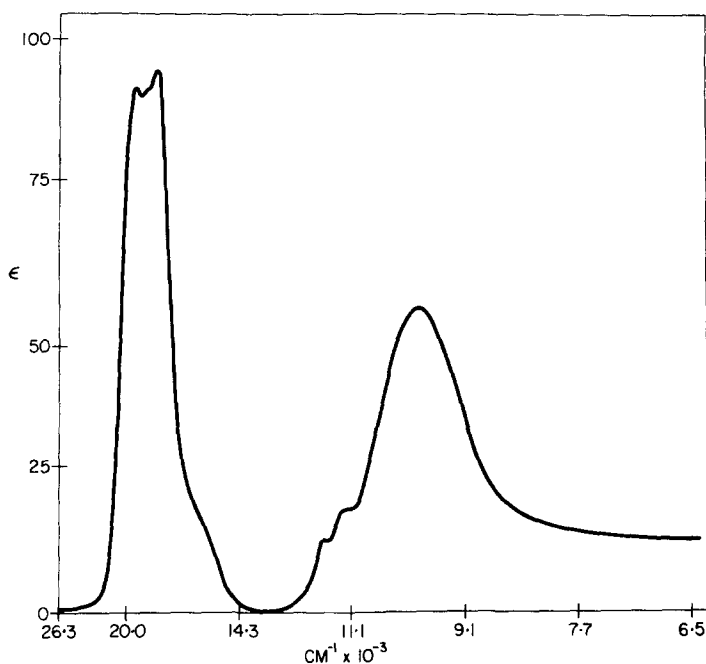

Fig. 4. Electronic spectrum of Ni(EDM)Cl$_2$ in chloroform.

The magnetic moments for the three complexes are of the high spin type ranging from 3·32 B.M. for iodide complex to 3·34 B.M. for the bromide to 3·40 for the chloride.

The instability of the bromide and iodide complexes can be rationalized by considering the steric requirements of the EDM ligand. In the Co(II) chloride complex[19] it has been shown that there are severe steric interactions between the chlorides and the two morpholine rings. Thus it would be expected that going to the larger anions, i.e., bromide and iodide that these interactions would increase

25. A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* **6**, 134 (1959).
26. F. A. Cotton and D. M. L. Goodgame, *J. Am. chem. Soc.* **82**, 5771 and 5774 (1960).

leading to the subsequent decrease in stability. From a comparison with the other complexes of bulky amines referred to in the introduction, it appears that EDM has the greatest tendency to force tetrahedral geometry, of the ligands of this class.