

STRUCTURAL INFORMATION ON NICKEL(II) AND ZINC(II) ACETATE COMPLEXES WITH HEXAMETHYLENETETRAMINE

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ABSTRACT

1 : 2 Coordination compounds formed by the interaction of nickel(II) and zinc(II) acetates with hexamethylenetetramine—a potentially tetradentate ligand—have been prepared and characterized by magnetic susceptibility, electronic and infrared spectral studies in the solid state. It is shown that hexamethylenetetramine, though a potentially tetradentate ligand, acts only as a terminally bonded monodentate ligand retaining the chair configuration of the uncoordinated molecule in these complexes. Infrared frequencies due to acetate groups indicate that they are present as terminally bonded monodentate ligands in the zinc(II) complex and bidentate chelating ligands in the nickel(II) complex. Tentative stereochemistry of the complexes in the solid state is discussed.

ALTHOUGH complexes of divalent metal salts with hexamethylenetetramine (Hmta) have received some attention¹⁻³ there is no report on those of metal acetates with this potentially tetradentate ligand. The present study on the preparation, magnetic susceptibility, electronic and i.r. spectral features of the coordination compounds formed by the interaction of nickel(II) and zinc(II) acetates with Hmta has been undertaken to elucidate the mode of bonding of Hmta, of the acetate groups and the tentative stereochemistry of the complexes isolated in the solid state.

Hmta was obtained from Dr. Theodor Schuchardt GmbH & Co., Munich and used as such. Complexes of nickel(II) and zinc(II) acetates were obtained by mixing together hot solutions of the appropriate metal(II) acetate and Hmta in ethanol. The mixtures were concentrated and then allowed to stand at room temperature. The complexes which crystallized out were filtered, washed with ethanol and dried at $\sim 80^\circ\text{C}$. Stoichiometries of the complexes isolated were established by standard analytical methods. $\text{Ni}(\text{Hmta})_2(\text{OAc})_2$: m.p. 110°C . Found: Ni, 13.10; C, 42.30; N, 24.61; Calc.: Ni, 12.91; C, 42.01; N, 24.51%. $\text{Zn}(\text{Hmta})_2(\text{OAc})_2$: m.p. 230°C . Found: Zn, 13.72; C, 42.00; N, 24.35. Calc.: Zn, 13.66; C, 41.64; N, 24.29%. Electronic spectrum of the nickel(II) complex was recorded as nujol mull in the range $33000\text{--}6000\text{ cm}^{-1}$ on a Cary 14 spectrophotometer. The mull was smeared on filter-paper and run against a reference consisting of a similar piece of filter paper soaked in nujol. Magnetic susceptibility was measured at room temperature by the Faraday's method with a Cahn R.G. Electro-balance Model 7550 using $\text{HgCo}(\text{NCS})_4$ as the magnetic susceptibility standard. Pascals' constants were used for diamagnetic

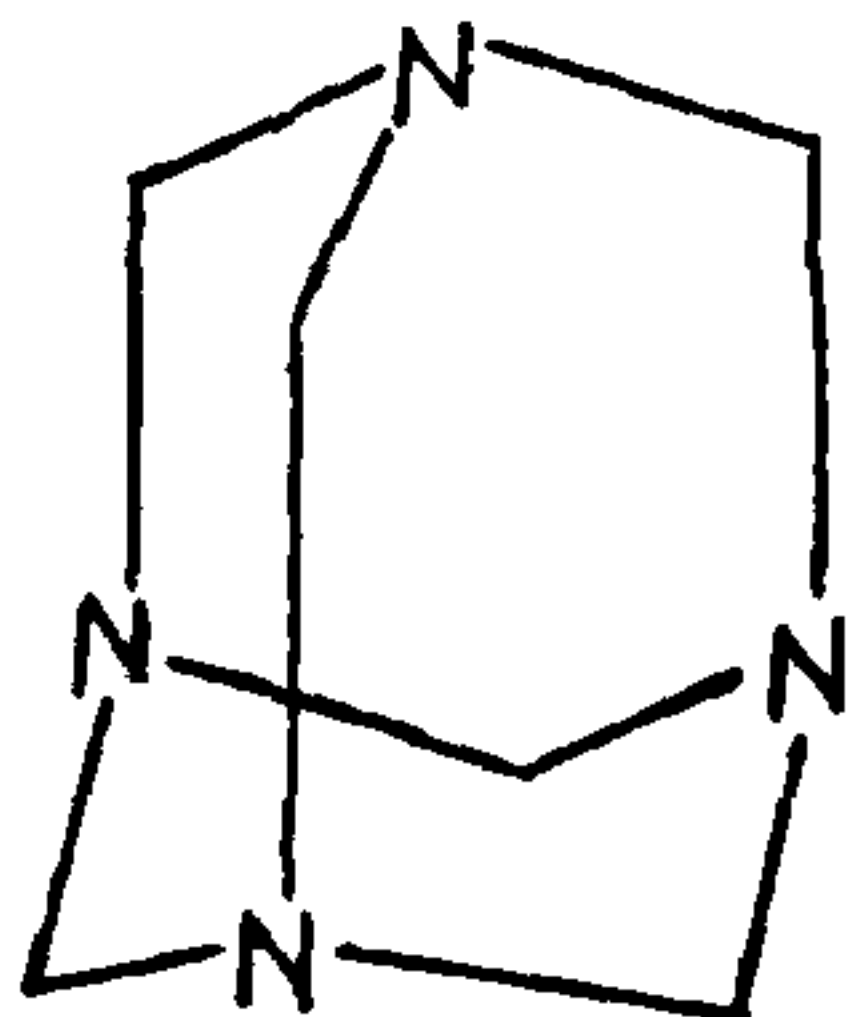
corrections. I.R. spectra of the uncoordinated Hmta and of the complexes were recorded as nujol mulls supported between sodium chloride plates (rock salt region) and thin polythene sheets ($650\text{--}200\text{ cm}^{-1}$) on a Perkin-Elmer 621 spectrophotometer equipped with caesium iodide optics.

Nickel(II) and zinc(II) acetates formed 1 : 2 complexes with Hmta. Manganese(II), cobalt(II), copper(II) and cadmium(II) acetates did not either react or did not give stoichiometric complexes with Hmta under similar conditions. Comparison of the i.r. spectra of the uncoordinated Hmta and of the metal(II) halide and pseudohalide complexes with this ligand facilitated the assignment of bands due to acetate groups. Strong bands due to acetate groups superimpose and mask some of the bands due to Hmta moiety. No absorption bands were observed which could be attributed to water, or ethanol in any of these spectra thus establishing that these complexes are anhydrous and free from coordinated or lattice water/ethanol.

Hexamethylenetetramine, a heterocyclic system having three fused rings in the chair configuration, possesses four bridge-head nitrogen atoms as the donor sites. The chemical and steric equivalence of the four nitrogen atoms has been demonstrated by various physico-chemical methods⁴. It may thus act as a mono-, bi-, tri- or tetra-dentate ligand. Recent studies on the coordination compounds formed by this potentially tetradentate ligand with metal salts have shown that Hmta acts only as (i) a terminal monodentate, or (ii) a bidentate ligand bridging between two metal ions. Of the several bands in the $1300\text{--}200\text{ cm}^{-1}$ region i.r. spectrum of this ligand, two strong bands at 1225 and 1000 cm^{-1} are assigned⁵ to νCN . Both these bands are split up into two well-defined and well separated bands in complexes in which Hmta acts as a bidentate ligand bridging between two metal ions⁶. Molecular models show that

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Hmta is more likely to bond to different metal ions and thus act as a bridging rather than a chelating ligand. (If chelated the coordinated Hmta must have a boat or cis configuration and i.r. spectra of such complexes would be anticipated to exhibit multiplicity of bands owing to the increased number of i.r. active fundamentals, cf. chelated 1,4-dioxane⁷). However, complexes in which Hmta molecule(s) act as monodentate ligand(s) bonding through only one of the four nitrogen atoms, both the ν_{CN} bands suffer only a very minor splitting resulting in closely spaced doublets or triplets.⁸



Infrared spectra due to coordinated Hmta in the 1:2 nickel(II) and zinc(II) acetate-Hmta complexes exhibit only very minor splitting of the ν_{CN} bands at 1225 and 1000 cm^{-1} resulting into closely spaced doublets/triplets and except for the slight shifting of some bands and some intensity changes are almost superimposable on the i.r. spectrum of uncoordinated Hmta. These features clearly indicate the exclusive presence of terminally bonded monodentate⁸ Hmta molecules retaining the chair configuration of the uncoordinated⁹ Hmta in both these complexes. Although a potentially tetradentate ligand stereochemically Hmta seems to act only as a terminally bonded monodentate ligand bonding through only one of its four nitrogen atoms to the nickel(II) and zinc(II) retaining the chair configuration of the uncoordinated ligand in the metal acetate complexes studied here.

Ideally coordination by the acetate groups is sought in their i.r. spectra where it is possible to distinguish between ionic, non-coordinated and coordinated species¹⁰. The free acetate ion has a very low symmetry, C_{2v} , and has fifteen fundamental vibrations all of which do show up both i.r. and Raman spectra. Significant i.r. vibrations due to the acetate group are: $\nu_{asym} \text{OCO}$, $\nu_{sym} \text{OCO}$ and δOCO . For unidentate coordination the $\nu_{asym} \text{OCO}$ and $\nu_{sym} \text{OCO}$ absorb at ~ 1520 and 1410 cm^{-1} . In the case of bidentate coordination these frequencies absorb with a separation of ~ 120 – 150 cm^{-1} . On the other hand, bridging acetate ligands

exhibit the $\nu_{asym} \text{OCO}$ at 1610 – 1580 cm^{-1} and the separation between the two stretching modes is higher, ~ 150 – 200 cm^{-1} owing to the lowered symmetry of the acetate group^{10,11}.

Nickel(II) Complex

The 1:2 nickel(II) acetate-Hmta complex is green in colour and has a room temperature magnetic moment of 3.5 B.M. which definitely rules out the presence of square planar nickel(II)¹². The electronic spectrum (in nujol) of this complex exhibits absorption bands at 8265, 14190 and 24690 cm^{-1} . The nickel(II) ion has a d_8 configuration which gives rise to ${}^3A_{2g}$ ground state in a regular octahedral field and absorption bands at ~ 8500 , 13500 and 25000 cm^{-1} corresponding to the excited states ${}^3T_{2g}$, ${}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$, respectively, are considered characteristic of nickel(II) in such an environment¹³. The observed bands in the electronic spectrum of this complex are assigned as: ${}^3A_{2g} \rightarrow {}^3T_{2g}$ 8265 cm^{-1} ν_1 , ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ 14190 cm^{-1} ν_2 , and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ 24690 cm^{-1} ν_3 . The frequencies of these bands agree well with those predicted from the Liehr and Ballhausen energy level diagram for nickel(II) in an octahedral field¹⁴. From the observed bands the value of $10 Dq$ (8265 cm^{-1}) is taken as the lowest energy transition ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and B the Racah parameter is calculated from the relationship $B = (\nu_2 + \nu_3 - 30 Dq)/15 = 940 \text{ cm}^{-1}$. In addition to the ligand bands modified slightly on account of coordination (*vide supra*) i.r. spectrum of this complex exhibits absorption bands at 1550, 1400 and 672 cm^{-1} which are identified as $\nu_{asym} \text{OCO}$, $\nu_{sym} \text{OCO}$ and δOCO modes, respectively. The frequencies of these modes and the separation (150 cm^{-1}) of the $\nu_{asym} \text{OCO}$ and $\nu_{sym} \text{OCO}$ modes strongly suggest the exclusive presence of symmetrically coordinated bidentate chelating acetate ligands^{10,11} in this complex. From the considerations that (i) Hmta molecules are coordinated as terminally monodentate ligands retaining the chair configuration of the uncoordinated molecule, (ii) acetate groups are bonded as bidentate chelating ligands, (iii) room temperature magnetic moment value, and (iv) from the discussion of the electronic spectral and ligand field parameters the 1:2 nickel(II) acetate-Hmta complex is tentatively assigned to have a six-coordinated monomeric structure with an octahedral environment of two nitrogen atoms (from two terminally bonded monodentate Hmta molecules) and four oxygen atoms (from two bidentate chelating acetate ligands) around the nickel(II) ions in the solid state.

Zinc(II) Complex

Since the electronic spectral and magnetic moment studies are not possible in this case the characterization of this complex is based mainly on its analytical

and i.r. spectral data. In addition to the absorption bands indicating the presence of terminally bonded monodentate Hmta molecules (*vide supra*) strong absorption bands are observed at 1550, 1450 and 660 cm^{-1} in the i.r. spectrum of this complex. Such bands are neither observed in the uncoordinated Hmta nor in the metal (II) thiocyanate⁸ or nitrate¹⁵ complexes with this ligand. These new bands are assigned as $\nu_{\text{asy}} \text{OCO}$ (1550 cm^{-1}), $\nu_{\text{sy}} \text{OCO}$ (1450 cm^{-1}) and δOCO (660 cm^{-1}) modes due to coordinated acetato groups. The frequencies of these modes and the separation (100 cm^{-1}) of the $\nu_{\text{asy}} \text{OCO}$ and $\nu_{\text{sy}} \text{OCO}$ are consistent with the presence of terminally bonded monodentate acetato ligands^{10,11} in this complex. Based on the considerations that (i) Hmta molecules are coordinated as terminally bonded monodentate ligands retaining the chair configuration of the uncoordinated molecule, and (ii) acetate groups are bonded as terminal monodentate ligands, the 1:2 zinc(II) acetate-Hmta complex is tentatively assigned a monomeric four-coordinated structure with a tetrahedral environment of two nitrogen atoms (of the two Hmta molecules) and two oxygen atoms (of the two acetato ligands) around the zinc(II) ions in the solid state.

The authors thank Professor B. M. Shukla, Head of the Chemistry Department, B.H.U., for providing facilities.

1. Barbieri, G. A. and Calzolari, F., *Atti. Accad. Lincei*, 1911, 19, 594; Scagliarini, G. and Tartarini, G., *Ibid.*, 1926, 4, 287; Scagliarini, G. and Brasi, E., *Ibid.*, 1928, 7, 509; Scagliarini, G. and Cesari, C. C., *Gazz Chim Ital.*, 1934, 64, 742; Watt, G. W. and Machel, A. R., *J. Am. Chem. Soc.*, 1950, 72, 2801.
2. Gyunter, E. A. and Mel'rinchenko, L. M., *Z. Neorg. Khim.*, 1966, 11, 429; De-Dantis, P., Kovacas, A. L., Liquori, A. M. and Mazzrella, L., *J. Am. Chem. Soc.*, 1965, 87, 4955.
3. Allan, J. R., Brown, D. H. and Lappin, M., *J. Inorg. Nucl. Chem.*, 1970, 32, 2287.
4. Andersen, A. F., *Acta Cryst.*, 1957, 10, 107; Becka, L. N. and Cruickshank, D. W. J., *Ibid.*, 1961, 14, 1092.
5. Mecke, R. and Spiecke, H., *Ber.*, 1955, 88, 1997.
6. Negita, H., Nishi, Y. and Koga, K., *Spectrochim. Acta*, 1965, 21, 2144.
7. Ramsay, D. A., *Proc. R. Soc. (London)*, 1947, 190A, 562.
8. Ahuja, I. S., Singh, Raghuvir and Yadava, C. L., *Spectrochim. Acta*, 1981, 37A, 407.
9. Finar, I. L., *Organic Chemistry*, Longmans, London, 1973, Vol. I.
10. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edition, New York, John Wiley, 1977.
11. Curtis, N. F., *J. Chem. Soc., A*, 1968, 1579.
12. Figgis, B. N. and Lewis, J., *Prog. Inorg. Chem.*, 1964, 6, 37.
13. Lever, A. B. P., *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1968.
14. Liehr, A. D. and Ballhausen, C. J., *Ann. Phys.*, New York, 1959, 6, 134.
15. Ahuja, I. S., Singh, Raghuvir and Yadava, C. L., *J. Molecular Structure*, 1980, 68, 333.