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Short Communication

Use of Ethyl Oxamate for Syntheses of Oxamato(-1) and Novel μ-Oxamato(-2) Complexes

Panayotis Th. Veltsistas, Spyros P. Perlepes, Miltiadis I. Karayannis,**
and **John M. Tsangaris***

Department of Chemistry, University of Ioannina, GR-45110 Ioannina, Greece

Summary. The use of ethyl oxamate for the synthesis of inorganic oxamato complexes is reported. A reaction system leading to the preparation of the novel polymeric μ-oxamato(-2) complexes $[M(oxm)(H_2O)_2]_x$ (M = Cu, Zn, Cd), $[Co(oxm)(H_2O)_2]_x \cdot 0.5x\,H_2O$ and $[Ni(oxm)(H_2O)_2]_x \cdot x\,H_2O$ is described (H_2oxm = oxamic acid). Ethyl oxamate can also be used for the preparation of monomeric oxamato(-1) complexes.

Keywords. Ethyl oxamate; Oxamato inorganic complexes; μ-Oxamato bridges; Magnetic moments.

Der Einsatz von Ethyloxamat für die Synthese von Oxamato(-1) und neuen μ-Oxamato(-2)-Komplexen (Kurze Mitt.)

Zusammenfassung. Es wird der Einsatz von Ethyloxamat für die Synthese von anorganischen Oxamato-Komplexen beschrieben. Ein Reaktions-System für die Herstellung von neuen μ-Oxamato-(-2)-Komplexpolymeren: $[M(oxm)(H_2O)_2]_x$, (M = Cu, Zn, Cd), $[Co(oxm)(H_2O)_2]_x \cdot 0.5x\,H_2O$ und $[Ni(oxm)(H_2O)_2]_x \cdot x\,H_2O$, wird vorgestellt. Ethyloxamat kann auch für die Herstellung von monomeren Oxamato(-1)-Komplexen verwendet werden.

Oxamic acid ($H_2NCOCOOH$, H_2oxm) is a very interesting and versatile ligand in coordination chemistry because a) it coordinates as $Hoxm^-$ [oxamato(-1) complexes] to metal ions (after ionization of the carboxylic hydrogen) through one of the carboxylato O-atoms and the amide O-atom [1–3] forming 5-membered chelate rings, through one of the carboxylato O-atoms and the neutral amide N-atom [4], through both carboxylato oxygens in a chelated or bridging mode [5], as a monodentate $O_{carboxylato}$ ligand [5, 6], or as a tridentate bridging ligand using all its O-atoms [5, 7], b) it may coordinate as $Hoxm^-$ to platinum in the platinum-blue species (after amide ionization) through the deprotonated amide nitrogen [6], and c) both the carboxylic and amide hydrogens can be removed and doubly deprotonated oxm^{-2} complexes [oxamato(-2) complexes] prepared; the oxm^{-2} ion be-

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** Present address: Department of Chemistry, Indiana University, Bloomington, IN 47405, USA

Table 1. Physical properties, magnetochemical and ligand field[a] spectral data of the polymeric oxamato(-2) Co(II), Ni(II) and Cu(II) complexes

	$[\mathrm{Co}(oxm)(\mathrm{H_2O})_2]_x\cdot 0.5\,x\,\mathrm{H_2O}$	$[\mathrm{Ni}(oxm)(\mathrm{H_2O})_2]_x\cdot x\,\mathrm{H_2O}$	$[\mathrm{Cu}(oxm)(\mathrm{H_2O})_2]_x$
Color	pink	pale green	pale blue
Λ_M ($\mathrm{S\,cm^2\,mol^{-1}}$)[b]	5	2	3
μ_{eff} (BM)[c,d]	4.91	2.92	1.38
Ligand field ($10^3\,\mathrm{cm^{-1}}$)[e,f]	${}^4T_{1g}\to{}^4T_{1g}$ (P) 19.42 ${}^4T_{1g}\to{}^4A_{2g}$ 16.60 ${}^4T_{1g}\to{}^2T_{2g}$ (G)[g] 15.50 sh $10\,Dq = 8\,860\,\mathrm{cm^{-1}}$ $B = 852\,\mathrm{cm^{-1}}$ $\beta = 0.88$	${}^3A_{2g}\to{}^3T_{1g}$ (P) 24.10 ${}^3A_{2g}\to{}^3T_{1g}$ (F) 15.50, 13.89 ${}^3A_{2g}\to{}^1E_g$ 12.58 sh $10\,Dq = 9\,060\,\mathrm{cm^{-1}}$ $B = 768\,\mathrm{cm^{-1}}$ $\beta = 0.73$	d-d 15.44 sh, 13.51

[a] In the 29 400–11 200 $\mathrm{cm^{-1}}$ region

[b] Values of molar conductivity for $10^{-3}\,M$ solutions in *DMF* at 25°C

[c] Per metal ion

[d] Measured at room temperature

[e] Diffuse reflectance spectra

[f] Assignments for the Co(II) and Ni(II) compounds are given in O_h symmetry

[g] Spin-forbidden bands

haves as an $O_{\mathrm{carboxylato}}$, $N_{\mathrm{deprotonated\,amide}}$ bidentate chelate [8–15] or bridging [6] ligand, as a monodentate $N_{\mathrm{deprotonated\,amide}}$ ligand in the platinum-green species [6], or as a tetradentate (bis-bidentate) bridging ligand in binuclear complexes [16–20] which also contain other bidentate or tridentate chelate ligands. The μ-oxamato (-2) binuclear copper(II) complexes show exciting magnetic properties [16–20], because the μ-oxm^{-2} bis-bidentate skeleton has been found to be extremely effective in transmitting exchange interaction between the two copper ions which are more than 5 Å apart [19, 20]; the factors controlling the magnitude of the superexchange interaction have been studied in detail [21].

Hitherto polymeric μ-oxamato(-2) complexes have not been known. The synthetic routes available for the preparation of exclusively, i.e. without the participation of other organic ligands in the coordination sphere of the metal ion, oxamato(-2) complexes lead to monomeric complexes in which the oxm^{-2} ion acts as a bidentate chelate ligand [8–15]. Since polymeric complexes with oxm^{2-} bridges might present interesting magnetic behaviour, we have turned our attention to the synthesis of such complexes and herein report the successful attainment of this objective for Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

The preparation of the complexes is summarized in Eq. (1),

$$1\,x\,M\mathrm{Cl_2} + 1\,x\,\mathrm{H}\,oxm\,Et + 2\,x\,\mathrm{NaOH} + (1+n)\,x\,\mathrm{H_2O} \xrightarrow[70\text{–}80^\circ\mathrm{C},\ 3\text{–}8\ \mathrm{h}]{Et\mathrm{OH/H_2O}} [M(oxm)(\mathrm{H_2O})_2]_x\cdot n\,x\,\mathrm{H_2O} + 1\,x\,Et\mathrm{OH} + 2\,x\,\mathrm{NaCl}, \tag{1}$$

$$n = 0 \text{ for } M = \mathrm{Cu, Zn, Cd};\ n = 0.5 \text{ for } M = \mathrm{Co} \text{ and } n = 1 \text{ for } M = \mathrm{Ni}.$$

In a typical experiment to a filtered solution of H *oxm Et* (10.5 mmol) in hot ethanol (30 ml) was added a solution of $\mathrm{CuCl_2}$ (10.0 mmol) in water (20 ml) under stirring. Addition of 40.0 ml 0.5 *N* NaOH

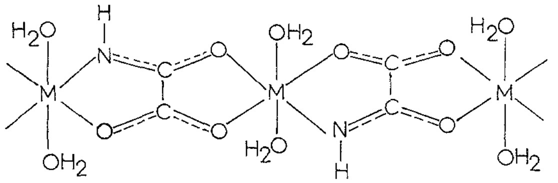
(20.0 mmol) and reflux for 3 h yielded a pale blue participate which was collected by filtration, washed with water, ethanol and acetone-ether 1 : 1 and dried in vacuo over P_4O_{10}.

Yields were between 80 and 90% based on the metal. The complexes are microcrystalline, stable in atmospheric conditions, and have a moderate solubility in *DMSO, DMF* and pyridine. The complexes were characterized by elemental analyses (*M*, H_2O, C, H, N), conductivity measurements, X-ray powder patterns, TG/DTG data, magnetic moments at room temperature and spectral (electronic, IR, far-IR, Raman for the Zn(II) and Cd(II) compounds) studies.

All the compounds are non-electrolytes in *DMF*. X-ray powder diffraction patterns indicate that the Zn(II) and Cd(II) compounds are strictly isomorphous. TG/DTG studies show the presence of both crystal and coordinated water in the Co(II) and Ni(II) complexes. The complexes decompose without formation of stable intermediates. The room temperature μ_{eff} values, d-d frequencies and the calculated ligand field parameters of the Co(II) and Ni(II) compounds are all characteristic of pseudo-octahedral high-spin stereochemistry [22, 23]. The electronic spectrum of $[Cu(oxm)(H_2O)_2]_x$ is fairly typical of a tetragonally distorted octahedral stereochemistry with a CuO_5N chromophore [23]. Its room temperature magnetic moment is subnormal, indicating the presence of antiferromagnetic interaction between Cu(II) ions [16–21].

The presence of bis-bidentate oxm^{2-} bridges in the structures of the prepared complexes is further supported by their vibrational spectra; the oxamato(-2) vibrational modes are observed at frequencies different from those of the monomeric complexes in which the oxm^{2-} ion behaves as a $O_{carboxylato}$, $N_{deprotonated\,amide}$ bidentate chelate ligand [8–15], but similar to those of the binuclear μ-oxm^{2-} compounds [16, 17, 19]. The most characteristic bands for the representative complex $[Ni(oxm)(H_2O)_2]_x \cdot xH_2O$ are as follows: $\nu\ (O-H)_{coord.\,water}$ at 3470 (s), $\nu\ (OH)_{crystal\,water}$ at 3330 (mb), $\nu\ (N-H)$ at 3200 (wb), $\nu\ (C=O)_{amide}$ at 1620 (vs), $\nu_{as}\ (COO^-)$ at 1595 (vsb), $\nu_s\ (COO^-)$ at 1358 (mb), δ (NH) at 1319 (s), $\nu\ (C-N)$ at 1270 (s), $\nu\ (C-C)$ at 830 (sh), π (NH) at 812 (sb) and $\nu\ (Ni-N) + \nu\ (Ni-O)$ at 377 (m), 359 (w) and 325 (sh) cm^{-1}. Satisfactory Raman spectra could only be obtained for the Zn(II) and Cd(II) complexes. The most intense bands appear at 1655, 1368 and 840 cm^{-1}, assigned to $\nu\ (C=O)_{amide}$, $\nu_s\ (COO^-)$ and $\nu\ (C-C)$ modes, respectively.

From the overall study presented it is concluded that the complexes have polymeric *trans*-pseudo-octahedral structures with apical water coordination (**I**).



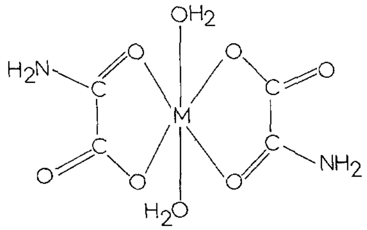
I

As a possible extension to the utility of H*oxmEt* for syntheses of oxamato complexes we have investigated whether this reagent could lead to H*oxm*$^-$ compounds and have found that it works extremely well. The known monomeric *trans*-octahedral centrosymmetric complexes $[Co(Hoxm)_2(H_2O)_2] \cdot 2H_2O$ and $[Zn(Hoxm)_2(H_2O)_2]$, available by another method [1, 2], and the new complexes

$[M(\mathrm{H}\,oxm)_2(\mathrm{H_2O})_2]$ (M = Mn, Ni, Cu) were prepared in high yields (~ 90%) by the reaction

$$1\,M\mathrm{Cl}_2 + 2\,\mathrm{H}\,oxm\,Et + 2\,\mathrm{H_2O} \xrightarrow[50^{\circ}\mathrm{C},\ 3\,\mathrm{h}]{Et\mathrm{OH/H_2O}} [M(\mathrm{H}\,oxm)_2(\mathrm{H_2O})_2] + 2\,Et\mathrm{OH} + 2\,\mathrm{HCl}. \quad (2)$$

The oxamato(-1) complexes were characterized by the same methods used for the study of the μ-oxamato(-2) complexes. We report some diagnostic data for $[\mathrm{Cu}(\mathrm{H}\,oxm)_2(\mathrm{H_2O})_2]$ which can be regarded as a representative complex for this series: Λ_M (*DMF*, 25°C) = $8\,\mathrm{S\,cm^2\,mol^{-1}}$; μ_{eff} (298 K) = 1.84 BM; d-d maximum (diffuse reflectance spectra) at 13 330 $\mathrm{cm^{-1}}$; IR data: $\nu\ (\mathrm{O-H})_{\mathrm{coord.water}}$ at 3 485 (m), $\nu_{as}\ (\mathrm{NH_2})$ at 3 419 (s), $\nu_s\ (\mathrm{NH_2})$ at 3 210 (m), $\nu\ (\mathrm{C=O})_{\mathrm{amide}} + \nu_{as}\ (\mathrm{COO^-})$ at 1 664 (vsvb), $\delta\ (\mathrm{NH_2})$ at 1 560 (m), $\nu\ (\mathrm{C-N})$ at 1 459 (m), $\nu_s\ (\mathrm{COO^-})$ at 1 320 (m), $\rho\ (\mathrm{NH_2})$ at 1 110 (s), $\delta\ (\mathrm{COO^-})$ at 880 (m), $\nu\ (\mathrm{C-C})$ at 839 (sh), $\omega\ (\mathrm{NH_2})$ at 821 (m), $\tau\ (\mathrm{NH_2})$ at 719 (m) and $\nu\ (\mathrm{Cu-O})$ at 367 (m), 330 (m) and 309 (sh) $\mathrm{cm^{-1}}$. The data for all the 1 : 2 oxamato(-1) complexes are consistent with structure (**II**).



II

In summary, synthetic high-yield access into polymeric μ-oxamato(-2) complexes, which represent a new class of oxamato complexes, has been achieved using H*oxmEt* as starting material. The utility of this reagent for the synthesis of monomeric oxamato(-1) complexes has also been emphasized.

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