Inorganica Chimica Acta, 53 (1981) L21–L22
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8-Quinolinol N-Oxide Adducts with 3d Metal(II) Perchlorates

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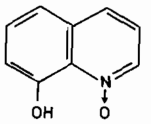
Received September 9, 1980

8-quinolinol N-oxide (I; qoH) behaves in a similar manner as the parent base (8-quinolinol or oxine), functioning as an anionic chelating agent (qo^-) towards a wide variety of metal ions [1]. Despite the pronounced tendency of qo^- to form $M(qo)_n$ chelates, most of the previous studies reporting on metal complex formation with this ligand involved the use of qoH as an analytical reagent for various metal ions [2], qualitative tests of complexing ability [3] or determination of stability constants of some $M(qo)_n$ chelates [4]. In addition, a few solid complexes of the $VO(qo)_2$ [5], $X_2Sn(qo)_2$ (X = F, Cl, Br, I, C_6H_5), $(C_6H_5)_2Sn(NCS)(qo)$ [6], $MoOCl(qo)_2$, $MoO_2(qo)(pyridine)$ and $Mo_2O_2Cl_4(qo)_2$(*o*-phenanthroline) [7] types were prepared and characterized. It was not till very recently that Ghuge *et al.* made a systematic synthetic and characterization study of a whole series of $M(qo)_n$ (M^{n+} = Be^{2+}, Mn^{2+}, Cu^{2+}, VO^{2+}, MoO_2^{2+}, UO_2^{2+}, $TiCl_2^{2+}$, $(C_2H_5O)_2Ti^{2+}$, Al^{3+}, Cr^{3+}, Fe^{3+}) chelates [8]. During the same work, a number of adducts of neutral qoH (namely $Sn^{II}Cl_2(qoH)_2$ and $Sn^{IV}Cl_4(qoH)_2$) were also reported [8]. In these laboratories, studies aimed at the syntheses and characterization of complexes formed by addition of neutral qoH to various metal perchlorates are underway. Our work concerning qoH adducts with divalent 3d metal perchlorates (M = Mn, Co, Ni, Cu, Zn) is reported in the present letter.


(I)

The synthetic procedure employed was as follows: 0.5 *M* solutions of the metal salt in ethyl acetate and of qoH in chloroform were dried over molecular sieve 4A, filtered and then combined at a ligand to metal molar ratio of 3:1. Precipitation was immediate in all cases. The precipitates were separated by filtration, washed with chloroform and anhydrous diethyl ether and stored *in vacuo* over anhydrous $CaSO_4$. The complexes analyze as $M(qoH)_4(ClO_4)_2 \cdot xH_2O$ (Table I; x = 4 for M = Mn, Cu, Zn; x = 6 for M = Co, Ni), and do not lose any water even after prolonged desiccation *in vacuo*. The infrared spectra of the new complexes favor the presence of exclusively ionic perchlorate (single ν_3 and $\nu_4(ClO_4)$ bands at *ca.* 1100 and 625 cm^{-1}, respectively, and very weak absorption in the $\nu_1(ClO_4)$ region, *i.e.*, at *ca.* 920 cm^{-1}) [9]. In the ν_{OH}(water) region, the ν_{OH} mode of coordinated water appears at 3420–3300 cm^{-1}, as a medium to strong broad maximum [10] on top of a weaker extremely broad absorption (at 3600–3100 cm^{-1}), which is obviously due to the simultaneous presence of lattice water [11] in the complexes reported. Ligand bands at 1525, 1275 and 887 cm^{-1},

TABLE I. Analyses, Magnetic Properties (294 K) and Molar Conductivities (10^{-3} *M* nitromethane solutions at 25 °C) of $M(qoH)_4(ClO_4)_2 \cdot xH_2O$ Complexes (x = 4 for M = Mn, Cu, Zn; x = 6 for M = Co, Ni).

M	Color	Analysis, Found (Calc.) %					$10^6 \chi_M^{cor}$, cgsu	μ_{eff}, μ_B	Λ_M, Ω^{-1} cm^2 mol^{-1}
		C	H	N	Metal	Cl			
Mn	Olive-yellow	44.06 (44.55)	3.55 (3.74)	5.43 (5.77)	5.46 (5.66)	7.05 (7.31)	15,548	6.07	160
Co	Khaki-brownish	42.96 (42.79)	3.92 (3.99)	5.56 (5.54)	5.85 (5.83)	7.04 (7.02)	11,082	5.13	171
Ni	Olive green	43.22 (42.80)	3.83 (3.99)	5.57 (5.54)	5.56 (5.81)	6.71 (7.02)	4780	3.37	179
Cu	Light olive green	43.75 (44.16)	3.63 (3.71)	5.48 (5.72)	6.37 (6.49)	7.11 (7.24)	2011	2.18	175
Zn	Light olive-yellow	43.91 (44.08)	3.76 (3.70)	5.46 (5.71)	6.89 (6.66)	7.47 (7.23)	Diamagnetic		158

involving contribution of deformation modes of the phenolic hydroxyl group, appear virtually unaltered in the spectra of the new complexes, thus confirming the presence of neutral qoH ligands [8]. Among five bands that may be associated with the ν_{N-O} mode (medium to strong bands at 1334 and 1310 cm^{-1}, two medium shoulders at 1284 and 1260 cm^{-1}, and the strong, sharp maximum at 1275 cm^{-1}, which includes δ_{OH} contribution) in the spectrum of free qoH, none is shifted appreciably upon metal complex formation (shifts not exceeding 2–3 cm^{-1} were generally observed); actually, the patterns of these five bands are virtually identical in the spectra of free qoH and the new $M(ClO_4)_2$ complexes. This is probably indicative of the presence of exclusively non-coordinated N–O oxygen sites in the qoH ligands of the complexes [8, 12]. In the lower frequency IR region (450–250 cm^{-1}), the free ligand shows two main bands at 430 and 350 cm^{-1}, which do not undergo any significant shifts upon metal complex formation. Medium to weak metal-sensitive bands appear as follows: M = Mn: 390, 277; M = Co: 414, 303; M = Ni: 420, 306; M = Cu: 417, 310; M = Zn: 381, 270 cm^{-1}. The bands at 420–381 cm^{-1} are tentatively assigned as ν_{M-O}(aqua) [10, 13], whilst those at 310–270 cm^{-1} are obviously due to the ν_{M-O} (phenolic oxygen) vibrational mode [14]. It is evident that the ν_{M-O} (N–O) vibration, which occurs at 380–320 cm^{-1} in the spectra of hexacoordinated 3d M^{2+} complexes with pyridine N-oxide and derivatives [15], is absent from the spectra of the new complexes.

The overall IR evidence favors coordination of qoH as a unidentate ligand, through the phenolic rather than the N–O oxygen. It should be noted, in this connexion, that Ghuge *et al.* also did not observe any significant shifts of ν_{N-O} in the spectra of Sn^{2+} and Sn^{4+} chloride adducts with qoH, and suggest that the ligands appeared to function as unidentate [8]. Furthermore, in several metal complexes involving the neutral form of the parent base (qH), coordination through the phenolic oxygen rather than the ring nitrogen has been established [16, 17].

The solid-state (Nujol mull) d–d transition spectra of the new Co^{2+}, Ni^{2+} and Cu^{2+} complexes are suggestive of hexacoordinated configurations, *viz.* (nm): M = Co: ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P), {}^4A_{2g}(F)$ 492 m,b, 555m,b; $\rightarrow {}^4T_{2g}(F)$ 1200 w,vb; M = Ni: ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 425 ms; $\rightarrow {}^3T_{1g}(F)$ 670 m,vb; $\rightarrow {}^3T_{2g}(F)$ 1180 w,vb (Dq = 847 cm^{-1}); M = Cu ${}^2E_g \rightarrow {}^2T_{2g}$ 775 m,vb (Dq = 1290 cm^{-1}). The ambient temperature magnetic moments (Table I) of the new complexes are generally normal for high-spin $3d^5$, $3d^7$ and $3d^8$ compounds or the $3d^9$ configuration. Molar conductivity measurements (Table I) show that the complexes behave as 1:2 electrolytes in nitromethane [18], as would be expected for species of the $[M(qoH)_4(OH_2)_2](ClO_4)_2 \cdot yH_2O$ type.

In conclusion, a number of complexes of the preceding type (y = 2 for M = Mn, Cu, Zn; y = 4 for M = Co, Ni) were synthesized and characterized as hexacoordinated, with cationic species involving MO_6 moieties. Four phenolic oxygen-bonded unidentate qoH and two aqua ligands occupy the first coordination sphere of the metal ions; the N–O oxygen site of qoH does not seem to participate in coordination.

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