Monatshefte für Chemie 113, 155—161 (1982)

Monatshefte für Chemie
Chemical Monthly
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Complexes of Oxamic Acid with Au(III) and Rh(III)

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(Received 21 July 1981. Accepted 6 August 1981)

The preparation and some properties of the deprotonated complexes of oxamic acid with Au(III) and Rh(III) are reported. On the basis of analytical results, conductometric measurements, magnetic moments and spectral data (IR and UV-visible), a square planar structure is proposed for $K[AuL(OH)_2]$ and octahedral for $K_3[RhL_3] \cdot 3\,H_2O$ (where LH_2 = oxamic acid). L^{2-} acts as a bidentate, non-bridging ligand.

[Keywords: Gold(III); Oxamato complexes; Primary amide; Rhodium(III)]

Komplexe der Oxamidsäure mit Au(III) und Rh(III)

Es wird über die Darstellung und einige Eigenschaften von deprotonierten Komplexen der Oxamidsäure mit Au(III) und Rh(III) berichtet. Auf der Grundlage von analytischen Ergebnissen, Leitfähigkeitsmessungen, magnetischen Momenten und IR- und UV(vis)-spektroskopischen Daten wird für $K[AuL(OH)_2]$ eine quadratisch planare und für $K_3[RhL_3] \cdot 3\,H_2O$ eine oktaedrische Struktur vorgeschlagen (LH_2 = Oxamidsäure). L^{2-} reagiert als zweizähniger, nicht überbrückender Ligand.

Introduction

Many studies have been made on the complexes of both carboxylic acids and primary amides. Complexes of ligands containing both of these functional groups have not been widely studied. The simplest such ligand is oxamic acid (LH_2 = $H_2NCOCOOH$).

Oxamic acid has tumor growth inhibition properties, mainly in its derivatives and salts[1]; this effect is probably due to the inhibition of action of lactic dehydrogenase. The spectral evidence indicates that

0026-9247/82/0113/0155/$ 01.40

LH_2 does not exist as the zwitterion in the solid state[2]. Laser *Raman* and IR spectra (4000–40 cm^{-1}) of crystalline LH_2 are consistent with hydrogen-bonded chains, which consist of alternate acid and amide dimeric units, each having a local center of symmetry[3].

Oxamic acid has interesting ligating possibilities, because a) it may coordinate as LH^- to the metal ions through both O-atoms[4] or one nitrogen and one oxygen[5] and b) the proton on the N-atom can be removed and deprotonated L^{2-} complexes prepared[6]. The synthesis of a binuclear Cu(II) complex with a μ-oxamato-bridge was reported recently[7].

The product of the reaction between $K_2[PtCl_4]$ and oxamic acid, the so called "platinum oxamate blue", is thought to consist of Pt-containing polyanions with a resultant Pt—Pt interaction along the polymeric or oligomeric chain[5, 8, 16].

As a continuation of our interest in the study of the metal-amide interactions[5, 6, 9], we studied the mode of bonding of oxamic acid coordinated to Au(III) and Rh(III).

Experimental

$K[AuL(OH)_2]$

A definite amount of $KAuCl_4$ (0.5 g) was treated with a 2 *M* $KHCO_3$ solution on a water bath, with constant stirring. At *pH* = 8 red-brown, hydrated Au_2O_3 precipitated according to the equation:

$$2\,KAuCl_4 + 6\,KHCO_3 \rightarrow Au_2O_3 \cdot 3\,H_2O + 6\,CO_2 + 8\,KCl$$

The reaction mixture was cooled to 15 °C and LH_2, in a ratio 1:2 Au(III) : LH_2, and 10% excess was added; this system was stirred vigorously and heated for 10 min. The resulting, clear, chestnut-brown solution (*pH* = 3-4) was cooled and kept at 0 °C without delay, otherwise metallic gold may precipitate as a result of a redox reaction between Au(III) and LH^-. Then a solution of 3 *M* KOH was added dropwise (*pH* was followed with a *pH*-meter). The addition of the base caused a rise in *pH* at first, followed by a fall, a fact indicating the gradual deprotonation of the amide group. The final *pH* should be 13. With the addition of the first portions of KOH the color changed from chestnut to dark brown. After 45 min (the time required for the completion of the reaction) the color was yellow-brown. At that point activated charcoal was added and the solution was shaken and filtered for removal of any suspensions. Precooled ethanol (20 ml) was added and, after stirring, a reddish-brown oily layer separated. The supernatant liquid was discarded and the layer was washed with cold ethanol (3 × 10 ml) and dried over P_4O_{10} in vacuum to yield chestnutred crystals of $K[AuL(OH)_2]$ (45%).

$K_3[RhL_3] \cdot 3\,H_2O$

To an aqueous Rh_2O_3 suspension (obtained as above from $RhCl_3 \cdot 3\,H_2O$) LH_2 was added in proportion 1 : 3 Rh(III) : LH_2 and a 10% excess; the mixture was refluxed for 3 h with stirring. The suspension dissolved gradually, yielding a bright orange-red solution ($pH = 3$-4):

$$Rh_2O_3 + 6\,H_2NCOCOOH \rightarrow 2\,Rh(H_2NCOCOO)_3 + 3\,H_2O$$

At 30 °C a solution of 3 M KOH was added in a quantity sufficient for the precipitation of Rh_2O_3 (final $pH = 13$). The solution was cooled to 15 °C:

$$Rh(H_2NCOCOO)_3 + 3\,KOH \rightarrow K_3[Rh(HNCOCOO)_3] + 3\,H_2O$$

The addition of cold ethanol resulted in the appearance of a yellow suspension, which changed to a viscous, oily layer, adhering to the bottom of the reaction flask. The mother liquor was removed and the product was washed with ethanol (3 × 10 ml). A very pure product was obtained by dissolving the precipitate in water and recrystallizing it with the addition of an equal volume of alcohol; this dried over P_4O_{10} in vacuum at 50 °C for 3 h to yield golden-yellow hygroscopic crystals of the desired product (65,5%).

Characterization

Gold was determined spectrophotometrically as $[AuBr_4]^-$, at $\lambda = 380$ nm, by dissolving the sample in concentrated HBr. Rhodium was determined spectrophotometrically, by the $SnCl_2$ method, at $\lambda = 475$ nm. C, H, N, K analyses and the physicochemical measurements were carried out as previously reported[5, 6, 9].

Results and Discussion

The preparation of $K[AuL(OH)_2]$ requires a low temperature, because the rate of degradation of the amidic bond is negligible (the *Nessler* test for ammonia is negative), although at this temperature one of the amidic hydrogens is ionized by the base. Both complexes, which gave very satisfactory elemental analyses, are highly crystalline substances, as revealed by a stereoscopic examination (1 × 400). They are soluble in water, *DMF* and *DMSO* and insoluble in ethanol, acetone and ether. The aqueous solutions of both complexes are alkaline ($pH = 9$-10). The addition of Ba^{2+}, Sr^{2+} and Ca^{2+} in aqueous solutions of $K[AuL(OH)_2]$ causes the formation of very insoluble precipitates of the general formula $M^{II}[AuL(OH)_2]_2 \cdot x\,H_2O$. From the Λ_M values obtained, we may conclude that $K[AuL(OH)_2]$ behaves in water as an 1 : 1 electrolyte, while $K_3[RhL_3] \cdot 3\,H_2O$ as a 3 : 1 one[10]. Some physicochemical data of the new complexes are given in Table 1.

The new complexes are diamagnetic. The visible-UV solution spectra of Au(III) and Rh(III) with oxamic acid may involve intraligand, charge transfer and d-d transitions which are found at decreasing energy and intensity. The visible absorption spectra of Rh(III) complexes may be expected to consist of transitions from the $^1A_{1g}$ ground state to other singlet states. Although the entire energy-level

Table 1. Λ_M *values, effects of heat and uv-visible spectral properties of the complexes*

Complex	Λ_M[a]/S cm^2 mol^{-1}	Effect of Heat/°C	λ_{max}/nm[b]	Assignments[c]	Comments
K[AuL(OH)$_2$]	110	The crystals begin to blacken in the 100-110 region due to separation of Au° and fulminating gold; the latter decomposes explosively at 150, yielding Au°, N_2 and NH_3	327 312	charge-transfer	square planar
K_3[RhL_3]·3 H_2O	378	The color changes to brown-black in the 190-200 and at 240 the decomposition commences with small explosions and evolution of NH_3	405 355 sh, 315 280	$^1A_{1g} \rightarrow {}^1T_{1g}$ $^1A_{1g} \rightarrow {}^1T_{2g}$ charge-transfer	pseudo-octahedral

[a] Values of molar conductance for ca. 10^{-3} *M* solutions at 25 °C (the compounds were assumed to be monomeric).
[b] In aqueous solutions.
[c] The spectra are interpreted and assigned on the basis of simple ligand field considerations; sh = shoulder.

Table 2. *Some characteristic and diagnostic IR frequencies (cm^{-1}) of oxamic acid and oxamato complexes*

Assignment[a]	$H_2NCOCOOH$	$KAu(C_2O_3NH)(OH)_2$	$K_3Rh(C_2O_3NH)_3 \cdot 3H_2O$
$\nu O{-}H$		3 420 s	3 600-3 150 m, vb
$\nu_{as}N{-}H$	3 350 s	d	d
$\nu_{s}N{-}H$	3 242 s	d	d
$\nu(O{-}H)_{acid}$	2 880 w, 2 760 w, 2 685 w, 2 540 w, 2 450 w	e	e
$\nu(C{=}O)_{acid}$	1 740 m		
$\nu(C{=}O)_{acid}$[b]	1 675 m, b		
$\nu C{=}O$		1 685 m, 1 600 m	1 625 s
$\delta(NH_2)$[c]	1 595 m	e	e
$\pi(OH)$	985 vs	e	e
$\nu C{-}C$	839 m	864 m, 843 m	833 m, 818 s
$\omega(NH_2)$	819 s	e	e
$\pi(NH)$		770 m	775 m
$\tau(NH_2)$	753 vs	e	e
$\rho(CO_2)$	332 m	e	e
ω(skel)	317 w		
Metal-ligands		410 w, 255 m, 230 m	360 m, 319 w, 304 w, 235 m

[a] Tentative and from Refs.[2, 3, 6]. [b] Amide I. [c] Amide II. [d] Obscured. [e] Absent.

vs = very strong, s = strong, m = medium, w = weak, vb = very broad, b = broad, ν_{as} and ν_s = antisymmetric and symmetric stretching, δ = in-plane deformation, π = out-of-plane bending, τ = torsion, ω = wagging, ρ = rocking.

pattern for Rh(III) is not known in full detail, the two absorption bands at 405 and 315 nm, found in the spectrum of $K_3[RhL_3] \cdot 3\,H_2O$ may represent transitions to the upper states $^1T_{1g}$ and $^1T_{2g}$[11]. Thus, the inherent tendency of the octahedral d^6 configuration to adopt the low-spin t_{2g}^6 arrangement, together with the relatively high ligand field strengths in these complexes of tripositive higher-transition-series ions as well as the fact that the $4d^6$ configuration is more prone to spin-pairing than the $3d^6$ one, provide a combination of factors that evidently leaves no possibility of there being any high-spin octahedral complex of Rh(III).

Table 2 gives some characteristic and diagnostic IR bands of oxamic acid and its complexes. In the νO—H region the spectrum of $K_3[RhL_3] \cdot 3\,H_2O$ exhibits a very broad absorption, covering the whole 3 600-3 150 cm^{-1} region, and attributable to exclusively lattice water[12]. The non-existence of coordinated water is also confirmed by the absence of the rocking and wagging modes of water[13]. The νO—H in the spectrum of $K[AuL(OH)_2]$ appears as a strong band at 3 420 cm^{-1} [14].

The characteristic vibrational modes of the —OH (of LH_2) and —NH_2 groups are absent from the spectra of the complexes. The IR spectrum of LH_2 shows two strong bands at 3 350 and 3 242 cm^{-1}, which are due to the asymmetric and symmetric N—H stretching vibrations of the —NH_2 group[2, 3]. The νN—H band in the complexes is overlapped by the νO—H bands.

The νO—H of organic acids, in the monomeric state, is expected in the 3 500-3 000 cm^{-1} region, but strong hydrogen bonding in the solid state can cause lowering and broadening of the band. This band appears in the spectrum of LH_2 as the usual very broad absorption covering the 2 900-2 400 cm^{-1} region with several sub-maxima, which are also typical of O—H stretching modes. These bands disappear after chelation, for the complexes examined.

The carbonyl stretching region in the spectra of the complexes is different (Table 2). The motions of the carbonyl groups are likely coupled. The bands, at ca. 1 685, 1 600 cm^{-1} for $K_3[AuL(OH)_2]$ and at 1 625 cm^{-1} for $K_3[RhL_3] \cdot 3\,H_2O$ are due to these modes and are assigned simply as νC = O. However, *Wallace* and *Wagner*[2] observed only one very strong broad band at 1 606 cm^{-1} for $K_2[CuL_2]$; they assigned this band to an overlapping of both of the IR active νC = O modes. *Nakamoto* and *Armendarez*[15] observed a strong broad doublet in the 1 660-1 600 cm^{-1} region in the spectra of some oxamido chelates. The frequencies of the νC = O bands in our spectra rule out the existence of oxamato-bridges[7].

The region of the free ligand's spectrum between 450 and 225 cm^{-1} has only two bands at 332 and 317 cm^{-1}. This would indicate that other bands observed in this spectral region (Table 2) would be assignable to metal—ligands stretching frequencies.

Metal—ligand vibrations are difficult to assign on an empirical basis, since their frequencies are sensitive to the metal and often they couple with low frequency modes in metal chelates; some ligand vibrations, activated by complex formation, may appear in the same region as the metal—ligand vibrations. Of the several bands observed in the far-IR spectra, some may be assigned to νM-N, νM-O(L^{2-}) and νAu-OH.

On the basis of the overall evidence presented, we may conclude that oxamic acid, as L^{2-}, acts as a bidentate N,O non-bridging ligand. On these grounds 4-coordinate square planar and 6-coordinated octahedral arrangements of the [AuO_3N] and [RhO_3N_3] types can be suggested for K[Au(C_2O_3NH)($OH)_2$] and K_3[Rh($C_2O_3NH)_3$]·3 H_2O, respectively, in the solid state.

References

[1] *Baker B. P., Lecote W. W.*, J. Med. Pharm. Chem. **1960**, 633; *Plummer D. T., Wilkinson J. H.*, Biochem. J. **81**, 38 (1961); *Reynolds V. H., Fleming Jr. J. H., Richie R. E., Foster J. H., Colowick S. P.*, Surg. Forum. **14**, 128 (1963).

[2] *Wallace F., Wagner E.*, Spectrochim. Acta **34 A**, 589 (1978).

[3] *Tripathi G. N. R., Katon J. E.*, Spectrochim. Acta **35 A**, 401 (1979).

[4] *Pellingelli M. A., Tiripicchio A., Camellini-Tiripicchio M.*, Acta Cryst. **28 B**, 998 (1972).

[5] *Tsangaris J. M., Veltsistas P.*, Inorg. Nucl. Chem. Lett. **17**, 35 (1981).

[6] *Galinos A. G., Tsangaris J. M., Kouinis J. K.*, Z. Naturforsch. **32 b**, 645 (1977); ibid. **33 b**, 987 (1978); *Perlepes S. P., Zafiropoulos Th. F., Kouinis J. K., Galinos A. G.*, Inorg. Nucl. Chem. Lett. **16**, 475 (1980); Idem., Z. Naturforsch. **36 b**, in press.

[7] *Nonoyama K., Ojima H., Ohki K., Nonoyama M.*, Inorg. Chim. Acta **41**, 155 (1980).

[8] *Burness J. H.*, Inorg. Chim. Acta **44**, L49 (1980).

[9] *Tsangaris J. M., Perlepes S., Galinos A. G.*, Z. Naturforsch. **34 b**, 456 (1979); *Zafiropoulos Th. F., Perlepes S. P., Ioannou P. V., Tsangaris J. M., Galinos A. G.*, ibid. **36 b**, 87 (1981); *Galinos A. G., Perlepes S. P., Zafiropoulos Th. F., Ioannou P. V., Kouinis J. K.*, Mh. Chem., in press.

[10] *Dutt N. K., Nag K.*, J. Inorg. Nucl. Chem. **30**, 3273 (1968); *Cook D. H., Fenton D. E.*, J. Chem. Soc. Dalton **1979**, 810.

[11] *Cotton F. A., Wilkinson G.*, Advanced Inorganic Chemistry, 3rd ed. New York: Interscience. 1972.

[12] *Hass M., Sutherland G. B. B. M.*, Proc. Roy. Soc. London **236 A**, 427 (1956).

[13] *Ichida K., Kuroda Y., Nakamura D., Kubo M.*, Spectrochim. Acta **28 A**, 2433 (1972).

[14] *Haghighi S., McAuliffe C. A., Hill W. E., Kohl H. H., Friedman M. E.*, Inorg. Chim. Acta **43**, 113 (1980).

[15] *Armendarez P. X., Nakamoto K.*, Inorg. Chem. **5**, 796 (1966).

[16] *Arrizabalaga P., Castan P., Laurent. J.-P.*, Transition Met. Chem. **5**, 204 (1980).