Inorganica Chimica Acta
LETTER

Electronic structure of dioxolene adducts of rhodium(III) tetraazamacrocyclic complexes

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(Received January 2, 1991)

Transition metal complexes of *o*-dioxolene ligands are receiving considerable attention. The interest ranges from the understanding of the fundamental interactions between the metal ions and radicals [1, 2], to the study of electron transfer processes, which are also relevant to biological processes [3], to the synthesis of new magnetic materials [4].

We are interested in metal dioxolene complexes as building blocks for synthesizing molecular materials having predetermined physical properties and this requires an appropriate description of the metal–ligand interactions. We have attempted to achieve this goal through the characterization of complexes of general formula $[ML(diox)]^{n+}$, where M is a 3d metal ion, L is a polyazamacrocyclic ligand and diox is an *o*-dioxolene, either catecholato or semiquinonato [5–10]. The lack of any significant electronic delocalization within the metal dioxolene chelate ring allows a well defined description of the oxidation states of both the metal ions and the ligands, i.e. catecholate or semiquinonate, and, as a consequence, a simple interpretation of the magnetic and spectral properties of these derivatives is often possible. However it has been recently shown that this approximation does not hold for some ternary mononuclear and dinuclear ternary ruthenium–bipyridine–polyoxolene complexes [11–16], whose properties must be interpreted by assuming a substantial mixing of the metal and ligand frontier orbitals.

Since the existence of a delocalized electronic structure for the latter systems might in principle be due to the π-acceptor properties of the bpy coligand, we thought it appropriate to synthesize 4d-dioxolene derivatives with innocent coligands. In this frame we wish to report here the synthesis and the characterization of some dioxolene adducts of the rhodium(III)–CTH moiety (CTH = D,L-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and to compare their spectral properties and redox reactivity with those of the cobalt(III) analogues [7], we described recently. The dioxolene ligands used are 3,5-di-t-butylcatechol and 3,4,5,6-tetrachlorocatechol. Throughout this paper we will indicate the dinegative catecholate ligands, as DTBCat and TCCat, whereas the corresponding mononegative radical semiquinonates and neutral quinones will be indicated as DTBSQ and TCSQ, and DTBQ and TCQ, respectively.

Experimental

Materials

The complex $Rh(CTH)Cl_3$ (*cis* isomer) was prepared according to literature methods [17]. 3,5-Di-t-butylcatechol and 3,4,5,6-tetrachlorocatechol (Aldrich) were used as received.

Rh(CTH)(DTBCat)PF$_6$

$Rh(CTH)Cl_3$ (0.5 mmol) was added to a deaerated methanolic solution (30 ml) containing the stoichiometric amount of 3,5-di-t-butylcatechol. Solid KOH (1.0 mmol) was added and the suspension was gently refluxed for 0.5 h. The resulting yellow solution was allowed to cool at room temperature and mixed with an aqueous solution of KPF_6. The yellow precipitate was filtered, washed with cool water and then recrystallized from dichloromethane–pentane mixtures. *Anal.* Found: N, 7.22; C, 47.48; H, 7.64. Calc. for $C_{30}H_{56}F_6N_4O_2PRh$: N, 7.44; C, 47.87; H, 7.50%.

Rh(CTH)(TCCat)PF$_6$

This compound was synthesized in a similar fashion using tetrachlorocatechol as dioxolene ligand. *Anal.* Found: N, 6.99; C, 34.27; H, 4.86. Calc. for $C_{22}H_{36}Cl_4F_6N_4O_2PRh$ requires: N, 7.20; C, 33.95; H, 4.66%.

Physical measurements

Physical measurements were carried out as previously described [6].

Results and discussion

cis-$Rh(CTH)Cl_2^+$ reacts easily with catechols under alkaline conditions, the reaction being virtually complete within 10 min in refluxing methanol. Solid microcrystalline derivatives of formula Rh(CTH)-

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0020-1693/91/$3.50

(diox)PF_6 were isolated. They are diamagnetic and their IR spectra are virtually superimposable with those of the cobalt(III)–catecholate analogues [7]. These complexes, therefore, are formulated as Rh(CTH)(DTBCat)PF_6 (**1**) and Rh(CTH)(TCCat)PF_6 (**2**), respectively, with the dioxolene ligand acting as bidentate and the macrocycle being coordinated in a folded configuration.

The electronic spectra of **1** and **2** show (Fig. 1, Table 1) intense absorption bands at 32 500 and 31 000 cm^{-1}, respectively, to be assigned to internal catecholate transitions [6]. Further the spectra are characterized by a relatively weak absorption at 24 400 and 25 300 cm^{-1} for **1** and **2**, respectively. A shoulder at 28 800 cm^{-1} is also observed in the spectrum of **1**. Comparison with other *cis*-octahedral Rh(III)-(CTH) with bidentate oxygen donors [17, 18] leads to expect the first d–d transition ($^1A_{1g}$–$^1T_{1g}$ in O_h) in the range 27 500–29 000 cm^{-1}, so that the shoulder at 28 800 cm^{-1} should be reasonably assigned to this transition. The other band can thus be assigned to a ligand-to-metal charge transfer transition. The weak intensities in this case will be justified by the poor overlap of the orbitals involved in the charge transfer excitation (from an out-of-plane π^* to in-plane σ orbital). We suggest the latter hypothesis on the basis of the blue shift of the absorption bands on passing from the more easily oxidizable DTBCat to TCCat and comparison with the spectra of the cobalt(III) analogues, which show an identical behaviour for the charge transfer bands and a red shift for the d–d absorptions [7].

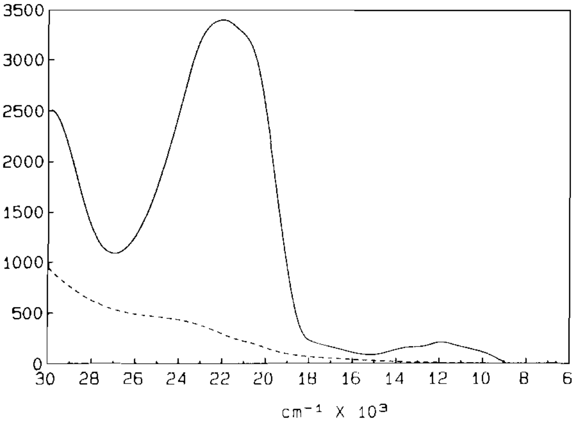

Fig. 1. Electronic absorption spectra of Rh(CTH)(DTBCat)$^+$ (- - -) and Rh(CTH)(DTBSQ)$^{2+}$ (——) in acetonitrile solution.

TABLE 1. Electronic spectra of Rh(CTH)(diox)$^{n+}$ complexes in acetonitrile ($n = 1, 2$)[a]

	DTBCat	TCCat	Assignment
Rh(CTH)(cat)$^+$	24.4(2.66)	25.3(2.52)	π^*(cat)–Rh(d_σ)
	28.8sh		d–d
	32.5(3.79)	31.0(2.70)	π^*(cat)–π^*(cat)
		32.0sh	
	38.5sh	38.5sh	π^*(cat)–π^*(cat)
Rh(CTH)(sq)$^{2+}$	10.0sh	8.6sh	
	11.4(2.24)	10.0(2.64)	n–π^*(sq)
	12.6sh	11.2sh	
	17.0sh		d–d($^2A_1$–$^2T_1$)
	21.5sh		Rh(d_π)–π^*(sq)
	22.2(3.52)	19.1(3.44)	Rh(d_π)–π^*(sq)
	29.4sh	27.3sh	π(sq)–π^*(sq)
	33.5(3.83)	30.7(3.76)	π^*(sq)–π^*(sq)

[a] In cm$^{-1} \times 10^3$; sh = shoulder; log ϵ in parentheses.

Cyclic voltammograms of deaerated acetonitrile solutions of **1** show two redox processes at −0.19 and 0.80 V versus the ferrocinium/ferrocene couple (Fc^+/Fc), the first being reversible and the latter non-reversible. Coulometric experiments indicate that both processes are monoelectronic. The reversible process is due to the ligand centered redox couple Rh(CTH)(DTBSQ)$^{2+}$/Rh(CTH)(DTBCat)$^+$, whereas the non-reversible one has to be reasonably assigned to the ligand centered redox couple Rh(CTH)(DTBQ)$^{3+}$/Rh(CTH)(DTBSQ)$^{2+}$. The observed behavior parallels those found for the analogue derivatives of 3d tripositive metal ions: as an example the cobalt(III) complex shows the same redox behaviour at −0.13 and 0.81 V versus Fc^+/Fc [7]. It should be pointed out that the electrochemical data show that the quinone derivative is not thermodynamically stable and rapidly decomposes. Apparently no redox processes involving the rhodium(III) ion are observed.

Similar conclusions can be drawn from the analysis of the voltammograms of solutions of **2**, which show a first reversible one-electron redox process at 0.40 versus Fc^+/Fc to be assigned to the Rh(CTH)(TCSQ)$^{2+}$/Rh(CTH)(TCCat)$^+$ redox couple and a non-reversible one at 1.28 V reasonably assigned to the Rh(CTH)(TCQ)$^{3+}$/Rh(CTH)(TCSQ)$^{2+}$ couple. As a comparison for the cobalt(III) analogue the same processes are found to occur at 0.48 and 1.43 V versus Fc^+/Fc [7].

Solutions containing the one-electron oxidation products of **1** and **2** were obtained by exhaustive electrolysis at 0.1 and 0.6 V versus Fc^+/Fc, respectively. The electronic spectra of both the solutions (Fig. 1, Table 1) show low energy transitions which have been seen to be diagnostic of the semiquinonate ligand [6]. Indeed the absorptions occurring at 11 400 and 10 000 cm^{-1} in the spectra of **1** and **2**, respectively, are assigned to the $9a_1$–$3b_1$ transition (n–π^* in character). Again as observed in other semiquinonate derivatives, both transitions show a vibrational progression presumably due to the C–O stretching mode [6–9]. These data, therefore, confirm that the one-electron oxidation products of **1** and **2** must be formulated as $Rh(III)(CTH)(DTBSQ)^+$ (**3**) and $Rh(III)(CTH)(TCSQ)^+$ (**4**) species.

Beside this characteristic band in the NIR region, the spectra of these species are characterized by three main absorptions in the visible and near ultraviolet region. The proposed assignment as reported in Table 1 has been made by comparison with the spectra of other semiquinonate derivatives. The broad intense band appearing at 22 200 and 19 200 cm^{-1} in the spectra of **3** and **4**, respectively, has been assigned to a metal to ligand charge transfer (t_{2g}–π^* SOMO) on the basis of its relatively low energy, high intensity, and its red shift on passing from the DTBSQ to the more electron-withdrawing TCSQ. A similar assignment may be proposed for other rhodium(III)-semiquinonate derivatives [19].

The weak absorption appearing as a shoulder at 17 000 cm^{-1} in the spectrum of **3** (in the spectrum of **4** it probably overlaps with the MLCT band) is tentatively assigned on the basis of its energy to the rhodium(III) spin forbidden $^1A_{1g}$–$^3T_{1g}$ (in O_h), made possible by strong exchange coupling between the triplet excited state of the metal ion and the radical ligand [8]. Indeed, as a result of this interaction this state will originate a quartet and a doublet and transitions involving the doublet ground state and the latter excited term will be allowed. As already discussed for chromium–semiquinonate derivatives, the close proximity of this transition to the intense charge transfer absorption may justify the observed intensity enhancement.

The EPR spectra at liquid nitrogen temperature of glassy solutions of **3** show an isotropic signal at $g = 2.00$ with $H_{pp} = 35$ G, whereas for solutions containing **4** an axial spectrum with $g = 2.007$ and $g = 1.987$ is observed. The latter behavior is apparently different from that observed for the cobalt(III) analogue. However for these rhodium derivatives the $\langle g \rangle$ values are substantially close to the $\langle g \rangle$ values characterizing the free radicals, and the observed deviations may be anticipated due to the large spin–orbit coupling constant of rhodium(III) [20–22]. The EPR spectra therefore show that these rhodium(III)–semiquinonato derivatives do not show any significant delocalization within the metal–dioxolene chelate ring. This behavior contrasts with that observed for the isoelectronic ruthenium(II)–semiquinonato derivatives, which are characterized by an extensive mixing of metal and ligand orbitals.

As a final remark, we wish to point out the different chemical properties of these two metal ions towards dioxolene ligands. From this work it is apparent that the rhodium(III) ion does not form stable quinone adducts, as evidenced by the electrochemical data. On the contrary stable complexes containing the ruthenium(II)–quinone moiety have been characterized [11, 13, 14, 16, 23]. It should be also pointed out that rhodium(III) form stable semiquinonato adducts. Contrasting with this behavior, the one electron oxidation of the tetraamino–catecholato–ruthenium(III) complex has been reported to yield the tetraamino–quinone–ruthenium(II) complexes as a result of an internal electron transfer [23].

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