Metal Complexes of 1,2-Diaminobenzene Derivatives. Determination of the Oxidation State of the Ligands through Crystallographic Data†

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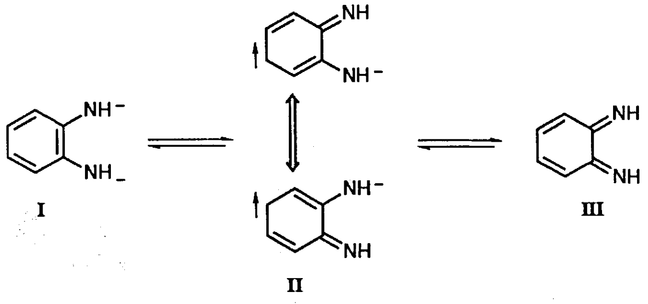
The known crystal structures of metal complexes containing 1,2-diaminobenzene derivatives in the form of the benzenediamine dianion **I**, benzosemiquinone diimine monoanion **II** or neutral benzoquinone diimine **III** have been examined. Since the forms **I**–**III** differ both in oxidation state and structural features, a simple method is proposed to correlate the oxidation states of these ligands with their structural parameters. It thus becomes possible to deduce the oxidation state of a 1,2-diaminobenzene derivative just by considering its crystal structure. The available data indicate that the 1,2-diaminobenzene derivatives considered, once complexed to a metal ion, generally do not assume charge-localized structures, like **I**–**III**, but intermediate ones. In most cases, these forms are near to **II** or intermediate between **II** and **III**. The results are compared with literature oxidation-state assignments, and discussed in terms of the back-bonding ability of the ligands.

Metal complexes derived from unsaturated chelating ligands are interesting because of their unusual chemical properties.[1–3] Increasing attention is being devoted to those derived from 1,2-diaminobenzene derivatives,‡ mainly because of their redox properties. In these compounds, the 1,2-diaminobenzene derivatives can be present as 1,2-diamine dianions **I**, 1,2-benzosemiquinone diimine monoanions **II**, or neutral 1,2-benzoquinone diimines **III** (see Scheme 1). These three forms are related by two one-electron oxidation-reduction steps, and their metal complexes often show intriguing 'electron-transfer series', in which either the metal and/or the ligands can be reduced or oxidized.[4] Although some complexes of 1,2-diaminobenzene derivatives were synthesised,[5] and their chemical[6] and electrochemical[4,7] properties have long been studied, most of the crystallographic analyses in this area were performed in the last few years.[8–19] The recent growth of crystallographic studies is due to the fact that knowledge of the crystal structure of metal complexes derived from non-innocent redox ligands is one of the best ways to assign oxidation states both to the metal and to the ligands. This is very well illustrated by the case of the *o*-quinone complexes, in which the redox series '*o*-quinone, *o*-semiquinone and catechol' is easily monitored by X-ray studies.[1,20]

Since the amount of crystallographic information on metal complexes derived from 1,2-diaminobenzene derivatives presently seems large enough to relate their structural features with their redox behaviour, in the present work we have attempted to formulate general rules for assigning an oxidation state to the ligands only by considering their structures. We took into account the known crystal structures of complexes containing the ligands **I**, **II** or **III**. By expressing the oxidation state of any given ligand by means of a comparison of its structural parameters with those of the 'pure' forms **I** and **III**, we obtained the dependences of the structural features on the oxidation state, thus allowing 'crystallographic monitoring' of the degree of reduction-oxidation within the series **I**–**III**.



Scheme 1

Experimental

Any 1,2-diaminobenzene derivative, once complexed to a metal ion, can assume one of the oxidation states represented by **I**, **II** or **III** (see Scheme 1), or an intermediate one. It is obvious that, ranging between **I** and **III**, the structural parameters of the ligand change considerably. Namely, while **I** has an aromatic character, **III** alternates between short and long bond distances, for example as in *o*-benzoquinones or in *o*-benzoquinone monooximes.[1,21] Moreover, it can be supposed that any 1,2-diaminobenzene derivative having the form **II**, or, more generally, an oxidation state intermediate between those of **I** and **III**, has structural parameters intermediate between those of the forms **I** and **III**. Therefore, we propose to evaluate the oxidation state of a given 1,2-diaminobenzene derivative by comparing its structural parameters with those of forms **I** and **III**. Since **I**, **II** and **III** have fairly rigid geometries, the most

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† *Supplementary data available* (No. SUP 56820, 7 pp.): experimental and calculated bond distances. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

‡ In the present work, '1,2-diaminobenzene derivatives' are regarded as having one of the formulae in Scheme 1; in the Tables they will be indicated as L, in addition the neutral ligand 1,2-diaminobenzene is denoted as H_2L.

sensitive structural changes varying between **I** and **III** are those related to the bond lengths, rather than to the bond angles, torsion angles, *etc.* Therefore, we compared the experimental bond distances of 1,2-diaminobenzene derivatives with those of model compounds having formulae **I** and **III**. Thus, for each of the eight bonds of a 1,2-diaminobenzene derivative, a function Δ_i can be defined as in equation (1) where d_i is the experimental

$$\Delta_i = 2(d_i - d_{\text{III}i})/(d_{\text{I}i} - d_{\text{III}i}) \qquad (1)$$

ith bond length of the derivative, and $d_{\text{I}i}$ and $d_{\text{III}i}$ are the ith bond lengths of the pure forms **I** and **III**. We assumed the average of the eight Δ_i, Δ, as being representative of the oxidation state of the given 1,2-diaminobenzene derivative. It is possible to regard this value as the number of electrons which have to be added to the molecule **III** to obtain the actual structure of the given ligand. In fact, **I** is formed through a two-electron reduction of **III**, and from equation (1) it appears that while a ligand isostructural with **III** has a Δ value of 0.0, a ligand isostructural with **I** has a Δ value of 2.0.

The eight Δ_i values were averaged by following the semiweighted mathematical model of ref. 22, since it has been verified that the environmental effects cannot be neglected when comparing the various d_i, $d_{\text{I}i}$ and $d_{\text{III}i}$. Therefore, the Δ values can be estimated as in equation (2) where W_i, the weights

$$\Delta = \Sigma W_i \Delta_i / \Sigma W_i \qquad (2)$$

corresponding to Δ_i, are given by equations (3) and (4) n (=8)

$$W_i = [\sigma^2(\mu) + \sigma^2(\Delta_i)]^{-1} \qquad (3)$$

$$\sigma^2(\mu) = [\Sigma(\Delta_i - \Delta_{\text{av}})^2/(n-1)] - \Sigma\sigma^2(\Delta_i)/n \qquad (4)$$

being the number of bonds taken into consideration. In equation (4) the quantity Δ_{av} is the unweighted mean of Δ_i, defined as in equation (5) and the quantity $\sigma^2(\Delta_i)$ is the variance

$$\Delta_{\text{av}} = \Sigma\Delta_i/n \qquad (5)$$

of Δ_i, taken as the highest value of the numerator and denominator of equation (1); the variances of the numerator and denominator of equation (1) were taken as the sum of the variances of the addenda.* Moreover, the standard error of Δ, $\sigma(\Delta)$, has been calculated as in equation (6).

$$\sigma(\Delta) = (\Sigma W_i)^{-\frac{1}{2}} \qquad (6)$$

The above mathematical model was applied to all the known crystal structures of 1,2-diaminobenzene derivatives complexed to metal ions, represented by an elemental formula $C_6H_6N_2$, like the molecules **I**–**III** shown in Scheme 1.[8–10,13–19] We disregarded all the ligands differing from **I**–**III** not only because they are not exactly in the same redox series, but also because a different extent of protonation of the amine/imine groups can imply significant differences in the structural features.[8,9,11,12,16,17] It is known, for example, that in the 1,2-diaminobenzene derivatives, while the aromatic C–NH_2 bond distance ranges between 1.391(3) and 1.408(2) Å,[24–27] the aromatic C–NH_3^+ bond length is longer and ranges between 1.445(11) and 1.476(13) Å.[26–30] Moreover, ligands of formula **I**–**III** show C–N distances ranging between 1.27(5) and 1.41(3) Å with a weighted average of 1.336(2) Å (weights = $1/\sigma^2$) and the neutral 1,2-diaminobenzene ligands complexed to metal ions show C–N distances ranging between 1.38(1) and 1.482(17) Å with a weighted average of 1.428(4) Å (weights = $1/\sigma^2$).

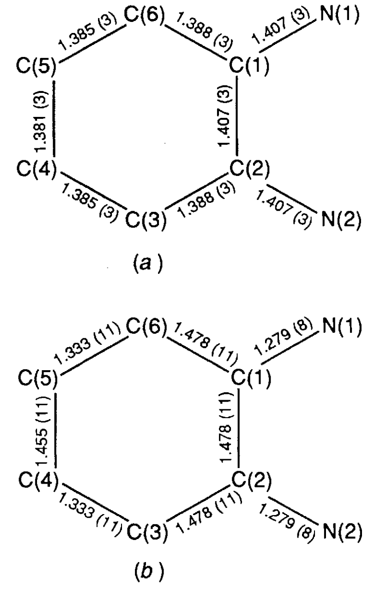

Fig. 1 (*a*) Bond lengths (Å) of 1,2-diaminobenzene taken from ref. 22. (*b*) Bond lengths of 1,2-benzoquinone diimine taken from ref. 31

In order to calculate Δ and $\sigma(\Delta)$ for the selected 1,2-diaminobenzene derivatives, it is necessary to know the values of $d_{\text{I}i}$ and $d_{\text{III}i}$ which have to be used in equation (1). In the case of $d_{\text{I}i}$, we chose the experimental bond lengths of uncomplexed 1,2-diaminobenzene,[25] and averaged the distances C(1)–N(1) and C(2)–N(2), C(1)–C(6) and C(2)–C(3), and C(5)–C(6) and C(3)–C(4) (*i.e.* we imposed a C_{2v} symmetry on the molecule). The choice of the uncomplexed 1,2-diaminobenzene might seem inconsistent with the previous observation that the extent of protonation of the amide groups can influence the geometry of the molecule. However, all the 1,2-diaminobenzene derivatives considered in the present paper are chelated to a metal ion. Thus, their bonding situation is somewhat more similar to neutral uncomplexed 1,2-diaminobenzene than to that of 1,2-benzenediamine dianion. In the case of $d_{\text{III}i}$, we chose the bond distances of a molecule assembled on the basis of the data reported in ref. 31, owing to the absence of suitable crystallographic information. The bond distances of these model compounds are reported in Fig. 1. Table 1 shows the Δ and $\sigma(\Delta)$ values calculated on the basis of the model compounds for all the 1,2-diaminobenzene derivatives considered.

To verify the correspondence of the oxidation states evaluated from the Δ values with the structural features of the 1,2-diaminobenzene considered, we compared the experimental bond distances with those calculated from equation (7). In order

$$d_{\text{calc}} = d_{\text{III}i} + [\Delta(d_{\text{I}i} - d_{\text{III}i})]/2 \qquad (7)$$

to stress this comparison, equation (7) was considered without the standard deviations of its addenda. The agreement between the experimental and the calculated bond distances was evaluated with the simple equation (8), where $d_{\text{exptl},i}$ and $d_{\text{calc},i}$

$$t = |d_{\text{exptl},i} - d_{\text{calc},i}|/\sigma(d_{\text{exptl},i}) \qquad (8)$$

are the experimental and calculated bond lengths and $\sigma(d_{\text{exptl},i})$ is the experimental standard deviation for the ith bond. The meaning of equation (8) is as follows:[32] the difference between the experimental and calculated bond distances is 'not significant' if $t < 1.960$, 'possibly significant' if $1.960 < t < 2.576$ and 'significant' if $t > 2.576$. The experimental and calculated bond distances and the agreement factors t (being quite consistently well below the threshold of 1.960) are

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* In the present paper, the published values of the estimated standard deviations (e.s.d.s) of the bond distances were multiplied by a factor 1.5, according to refs. 22 and 23.

Table 1 Values of Δ [equation (2)] and σ(Δ) [equation (6)] for the 1,2-diaminobenzene derivatives considered

Compound[a]	Ligand	Δ	σ(Δ)	Ref.
1 $[Cu(py)_2L]$	1	2.00	0.10	10
2 $[Co(py)L_2]Cl$	1	1.14	0.18	10
	2	0.76	0.20	10
3 $[RhCl(PPh_3)_2L]$	1	1.32	0.10	13
4 $[CoL_2]$	1	1.18	0.14	14
	2	1.54	0.14	14
5 $[CoClL_2]$	1	0.56	0.18	14
	2	1.22	0.12	14
6 $[Co(H_2L)L_2]$	1	0.82	0.32	16
	2	1.02	0.12	16
7 $[Ru(H_2L)L_2][PF_6]_2$	1	0.38	0.44	9
	2	0.48	0.50	9
8 $[FeL_3][PF_6]_2\cdot$thf	1	0.56	0.14	14
	2	0.60	0.16	14
	3	0.58	0.12	14
9 $[Ru(bipy)_2L][PF_6]_2$	1	0.92	0.12	15
10 $[Fe(CN)_4L]X$	1	0.80	0.10	18
11 $[NiL_2]$	1	1.60	0.12	19
	2	1.08	0.18	19
12 $[ReL_3][ReO_4]\cdot Me_2CO$[b]	1	1.24	0.26	8
	2	1.28	0.36	8
	3	1.04	0.42	8
	1′	0.54	0.54	8
	2′	0.62	0.42	8
	3′	1.42	0.22	8
13 $[ReL_3]\cdot$thf	1	1.46	0.20	8
	2	1.92	0.22	8
	3	1.44	0.28	8

[a] py = Pyridine; thf = tetrahydrofuran; bipy = 2,2′-bipyridine. [b] There are two crystallographically independent molecules in the asymmetric unit.

Table 2 Minimum (t_{min}), maximum (t_{max}) and mean ($\bar{t}$) values of the agreement factor t [equation (8)] and number of cases in which $t < 1.960$, $1.960 < t < 2.576$ and $t > 2.576$, for the bonds of the compounds studied

Bond	$\bar{t}$	t_{min}	t_{max}	$t < 1.960$	$1.960 < t < 2.576$	$t > 2.576$
C(1)–N(1)	0.858	0.000	3.353	24	3	1
C(2)–N(2)	1.002	0.121	3.118	25	2	1
C(1)–C(2)	0.681	0.015	3.000	25	2	1
C(2)–C(3)	0.832	0.000	3.000	26	1	1
C(3)–C(4)	0.789	0.038	3.000	25	2	1
C(4)–C(5)	0.670	0.038	4.000	25	2	1
C(5)–C(6)	0.614	0.000	1.538	28	0	0
C(6)–C(1)	0.790	0.000	2.833	27	0	1

given in SUP 56820. Moreover, Table 2 reports, for each of the eight bonds of a 1,2-diaminobenzene derivative, the minimum, maximum and mean values of the agreement factor t, calculated over all the 28 ligands considered. The number of cases with $t < 1.960$, that with $1.960 < t < 2.576$, and that with $t > 2.576$ are also reported for each of the eight bonds. It can be seen from these data that although the maximum value of t is often higher than the threshold 1.960 and/or 2.576, the mean value of t is always well below these thresholds. Moreover, the number of cases with $1.960 < t < 2.576$ and $t > 2.576$ is always negligible with respect to that with $t < 1.960$. This means that the experimental bond distances are in general statistically equal to those calculated with equation (7). Therefore, the agreement between the structural and redox changes can be considered satisfactory.

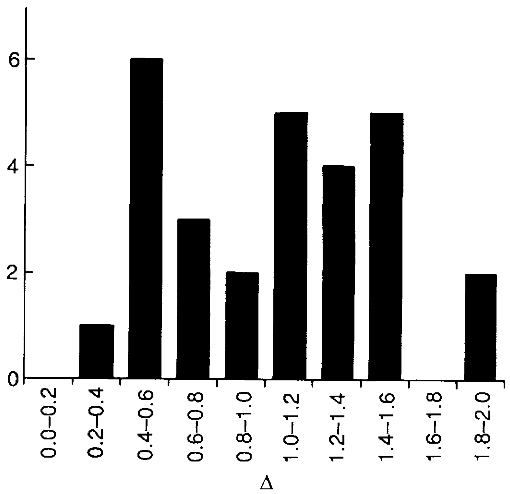

Fig. 2 Histogram showing the frequency of occurrence of Δ values [equation (2)] for Δ intervals of 0.2

Discussion

Fig. 2, a histogram of the distribution of Δ values for intervals of 0.2, shows that the 1,2-diaminobenzene derivatives do not tend to assume charge-localized structures. In other words, they cannot be conveniently described by the formulae **I**–**III**, but are in general intermediate between them. If we consider as representable by the formula **I** the ligands having $1.8 < \Delta < 2.0$, by **II** those having $0.8 < \Delta < 1.2$ and by **III** those having $0.0 < \Delta < 0.2$, we observe that no forms **III**, two forms **I** and seven forms **II** can be assigned to the 28 1,2-diaminobenzene derivatives considered. Ten are intermediate between forms **III** and **II**, and nine are intermediate between **I** and **II**. Once complexed to a metal ion, the 1,2-diaminobenzene derivatives are more similar to dithiolene compounds,[2] in the complexes of which the distribution of charge between the ligands and the metal is often ambiguous, than to the benzoquinones, which generally assume charge-localized structures.[1,20]

Fig. 2 also shows that most of the 1,2-diaminobenzene derivatives have Δ values ranging between 0.2 and 1.4 (21 cases out of 28). This means that they have a limited back-bonding acceptor ability. In fact, while the general synthetic procedure for complexing them to metal ions implies the use of the reduced 1,2-diaminobenzene as starting material, they are at least partially oxidized in the resulting metal complexes. However, their back-bonding acceptor ability is not nil. It has been observed by von Zelewsky and co-workers[15] that the amount of π-back bonding to the ligand is more important for a 1,2-diaminobenzene derivative than for 2,2′-bipyridine in complex **9**.

As a consequence of the tendency of the 1,2-diaminobenzene derivatives to assume delocalized ground states, some of the assignments of oxidation states found in the literature do not completely agree with ours. Namely, the formulae **I**–**III** have often been taken as actual representatives of the 1,2-diaminobenzene derivatives, and the possibility that these ligands can have intermediate forms has been disregarded.

This discrepancy is not very evident in the case of the ligands considered as having formula **II**, If we consider ligands having $0.8 < \Delta < 1.2$ as representable by this formula, the literature assignments (see Table 2) agree with those based on the Δ values in the following cases: **2**, ligand 1; **4**, ligand 1; **6**, ligand 1; and **6**, ligand 2 [Δ = 1.14(18), 1.18(14), 0.82(32) and 1.02(12)]. The other ligands considered in the past to be representable by formula **II**, have Δ values which in general do not deviate very much from the range $0.8 < \Delta < 1.2$: **2**, ligand 2; **3**, ligand 1; **4**, ligand 2; **5**, ligand 1; and **5**, ligand 2 [Δ = 0.76(20), 1.32(10), 1.54(14), 0.56(18) and 1.22(12)]. Moreover, the fact that in complex **9** the amount of π-back bonding to the ligands is more important for the 1,2-diaminobenzene derivative than for the 2,2′-bipyridines[15] is consistent with our assignment of a

Table 3 Comparison between 1,2-diaminobenzene derivatives bonded to the same metal centre, by means of the $t(\Delta)$ agreement factor [equation (9)]

Complex	Ligand A	Ligand B	$t(\Delta)$
2	1	2	1.412
4	1	2	2.092
5	1	2	3.051
6	1	2	0.585
7	1	2	0.150
8	1	2	0.188
8	2	3	0.100
8	1	3	0.108
11	1	2	2.404
12	1	2	0.090
12	1	3	0.405
12	2	3	0.434
12	1′	2′	0.148
12	1′	3′	2.173
12	2′	3′	1.687
13	1	2	1.547
13	1	3	0.058
13	2	3	1.348

benzosemiquinone diimine monoanion character to the ligand [$\Delta = 0.92(12)$]. It has been observed that the π bonding in complex **11** is delocalized through the ligand system, and that the slight differences in bond lengths within the benzene rings suggest a partial animic diimine character; this is consistent with our evaluation of the oxidation states of the ligands, implying an intermediate character between the forms **II** and **I** {Δ = 1.60(12) and 1.08(18); weighted average value = 1.44(10) (weights = $1/\sigma^2(\Delta)$]}.

The discrepancy between the oxidation-state assignments found in the literature and those evaluated by us on the basis of the Δ values is more evident in the case of 1,2-diaminobenzene derivatives which have been considered in the past as having formula **III** [**7**, ligand 1; **7**, ligand 2; **8**, ligand 1; **8**, ligand 2; **8**, ligand 3; and **10**, ligand 1]. Namely, if the ligands having $0.0 < \Delta < 0.2$ are considered to be representable by this formula, it can be seen that none of the 1,2-diaminobenzene derivatives considered is represented by **III** (see Table 2). It should be noted that the choice of the model compound for form **III** (see Fig. 1) is somewhat arbitrary, and it is therefore possible that the poor agreement between the Δ values calculated by us and the literature assignments of the oxidation state of form **III** depends on an inaccurate choice of the model compound for **III**. However, no direct experimental data are available and we did not find alternatives in ref. 31.

If we consider as representable by formula **I** the ligands having $1.8 < \Delta < 2.0$, there is a good agreement between the literature assignments of oxidation states and the Δ values calculated by us in the case of complex **1**, ligand 1 [$\Delta = 2.00(10)$], but poor in the case of the ligands in complexes **12** and **13**.

Although the crystal structures of complexes **12** and **13** are unfortunately poorly refined, and thus their significance in the present discussion is limited, it is interesting to use them to check the possible application of the assignments of oxidation states on the basis of the Δ values. Complex **12** has been described as a rhenium(VII) ion complexed by three 1,2-benzenediamine dianions **II**. However, on the basis of our results, this complex is better described as intermediate between a rhenium(IV) and a rhenium(V) ion bonded to three ligands roughly representable by formula **I**; considering as chemically equivalent the two crystallographically independent $[ReL_3]^+$ complexes, the six ligands have a weighted mean Δ value of 1.19(13) [weights $1/\sigma^2(\Delta)$] and therefore each of the two rhenium cations has a charge of 4.57(23). Complex **13**, obtained by a one-electron reduction of **12**, has been described as intermediate between a rhenium(VI) species containing three 1,2-benzenediamine dianions **I** and a rhenium(VII) species having an unpaired electron located mainly in ligand orbitals. However, on the basis of our results, this complex can be better described as a rhenium(V) ion complexed by three ligands intermediate between the formulae **I** and **II** (from a formal point of view, two of them in the form **I** and the third in form **II**); the three ligands have a weighted mean Δ value of 1.60(13) [weights = $1/\sigma^2(\Delta)$], and thus the rhenium cation has a charge of 4.80(23). Therefore, the one-electron reduction of complex **12** to **13** can be seen to resemble the bis(3,5-di-*tert*-butylbenzosemiquinone)-manganese(II)–bis(3,5-di-*tert*-butylcatecholato)manganate(III) and tris(3,5-di-*tert*-butylbenzosemiquinone)vanadium(III)–tris-(3,5-di-*tert*-butylcatecholato)vanadate(V) couples, where the reduction of the complex implies a change in the electronic distribution between the metal and the ligands and eventually leads to oxidation of the metal.[33,34]

Another intriguing consequence of the determination of the oxidation states of the 1,2-diaminobenzene derivatives through crystallographic data is the possibility to compare quantitatively the oxidation states of ligands co-ordinated to the same metal centre. In order to do that we used the significance test proposed by Cruickshank and Robertson,[32] defined as in equation (9). This test implies that the difference

$$t(\Delta) = |\Delta_1 - \Delta_2|/[\sigma^2(\Delta_1) + \sigma^2(\Delta_2)]^{\frac{1}{2}} \qquad (9)$$

between the two Δ values is 'not significant' if the agreement factor $t(\Delta) < 1.960$, 'possibly significant' if $1.960 < t(\Delta) < 2.576$, and 'significant' if $t(\Delta) > 2.576$. The results, summarized in Table 3, indicate that the differences between the oxidation states of the ligands bonded to the same cation are 'possibly significant' and 'significant' only in complexes **12** (ligands 1′, 3′), **4** and **11** [$1.960 < t(\Delta) < 2.576$], and **5** [$t(\Delta) > 2.576$]. In all the other cases the 1,2-diaminobenzene derivatives co-ordinated to the same metal centre are equivalent. The non-equivalence of non-innocent redox ligands within the same complex is not a common occurrence. As far as we know, the only well characterized analogous case is the complex (2,2′-bipyridine)(3,5-di-*tert*-butylcatecholato)(3,5-di-*tert*-butylsemiquinone)cobalt(III) whose structure has been determined in the solid state, and for which the results of magnetic, EPR, NMR and electronic spectral experiments in toluene solution indicate an equilibrium between a cobalt(II) species, (2,2′-bipyridine)bis(3,5-di-*tert*-butylsemiquinone)cobalt(II), and the cobalt(III) one mentioned.[35]

Acknowledgements

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