Dalton Transactions

PAPER

Cite this: DOI: 10.1039/c2dt32629a

Received 3rd November 2012, Accepted 22nd December 2012 DOI: 10.1039/c2dt32629a

www.rsc.org/dalton

Introduction

Mixed-valence chemistry has a long and rich history that is characterized by a strong interplay of experimental, theoretical and computational studies.¹⁻⁴ The results offer enhanced chemical insight into metal–ligand electron-transfer situations and suggest that mixed-valence materials may eventually be exploited in molecular electronics and molecular computing.⁵

Catechol oxidase is an enzyme with the type-3 active site that catalyzes the oxidation of a wide range of *o*-diphenols (catechols) to the corresponding *o*-quinones coupled with 2e/ $2H^+$ reduction of O₂ to H₂O, in a process known as catecholase activity.⁶⁻¹⁵ The generated *o*-quinones are autopolymerized producing a brown polyphenolic pigment, *i.e.* melanin, a process that is considered to protect damaged tissues against pathogens or insects. The crystal structure of the *met* form of the enzyme reveals that the active center consists of a hydroxobridged dicopper(n) center in which each copper(n) center is

^bUniversité Paris Descartes, Laboratoire de Cristallographie et RMN biologiques UMR 8015, Faculté de Pharmacie, 4 avenue de l'Observatoire, 75006 Paris, France †Electronic supplementary information (ESI) available: Tables S1–S4 and Fig. S1–S4. CCDC 908081–908083 for 1–3 respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32629a

Dinuclear mixed-valence Co^{III}Co^{II} complexes derived from a macrocyclic ligand: unique example of a Co^{III}Co^{II} complex showing catecholase activity†

Samit Majumder,*^a Suraj Mondal,^a Pascale Lemoine^b and Sasankasekhar Mohanta*^a

The work in this paper presents the syntheses, characterization, catecholase activity, and electrospray ionization mass spectroscopic (ESI-MS positive) study of three mixed-valence dinuclear Co^{III}Co^{III}Co^{III}Co^{III}C(N₃)₃)-CH₃CN (**1**), [Co^{III}Co^{III}C(O^{III}C)₃)-CH₃CN (**2**), and [Co^{III}CO^{III}C(P₄)(μ -CH₃COO)₂](ClO₄) (**3**), derived from a tetraimino diphenolate macrocyclic ligand H₂L, obtained on [2 + 2] condensation of 4-ethyl-2,6-diformylphenol and 2,2'-dimethyl-1,3-diaminopropane. While **1** and **2** are diphenoxobridged, **3** is a heterobridged bis(μ -phenoxo)bis(μ -acetate) system. Utilizing 3,5-di-*tert*-butyl catechol (3,5-DTBCH₂) as the substrate, the catecholase activity of all the three complexes has been checked in methanol/acetonitrile/*N*,*N*-dimethyl formamide. While **2** and **3** are inactive, complex **1** shows catecholase activity with turnover numbers of 482.16 h⁻¹ and 45.38 h⁻¹ in acetonitrile and methanol, respectively. Electrospray ionization mass (ESI-MS positive) spectra of complexes **1–3** have been recorded in acetonitrile solutions and the positive ions have been well characterized. The ESI-MS positive spectrum of complex **1** in the presence of 3,5-DTBCH₂ has also been recorded and, interestingly, two positive ions [Co^{III}Co^{III}L(N₃)₂(3,5-DTBCH⁻)H]⁺ and [Co^{III}Co^{III}L(μ -3,5-DTBCH²-)Na]⁺ have been identified.

> coordinated to three histidine nitrogens and adopts a trigonal pyramidal environment with one nitrogen in the apical site. The structure determination of catecholase oxidase has encouraged an extensive investigation on model compounds to understand the structure-property relationship.^{6a-c,7b-f,8-14} As the structure contains a dicopper(π) moiety, several dicopper(π) complexes derived from nitrogen containing dinucleating ligands have been mainly employed for this purpose. While the metallo-enzyme contains hydroxo-bridged dicopper(II), activity has been observed for dicopper(II) systems having hydroxo^{6a-c,11} or various other bridging moieties.^{6a-c,7a,d,8a,9,10} Again, although the enzyme contains a dicopper(II) moiety, a few monocopper(II) complexes and even a few copper(II) clusters and polymers have been found as active catalysts.¹¹ The catecholase activity of complexes of the ions of other metals such as Mn, Fe, and Co has also been observed.¹⁶⁻¹⁸ All these indicate that the exploration of the possibility of catalyzing catecholase activity by new types of species in terms of any of the following deserves importance: ligand environment, metal ion, metal ion combination, oxidation states of the metal ions, nuclearity of the complexes. Moreover, straightforward structure-property correlations are still lacking, indicating further that the problem of modelling the catecholase activity remains still open.

> Catecholase activity studies of complexes of metal ions, other than $copper(\pi)$, are very much less and therefore

RSCPublishing

View Article Online

^aDepartment of Chemistry, University of Calcutta, 92 A. P. C. Road, Kolkata 700 009, India. E-mail: sm_cu_chem@yahoo.co.in, samitmaj@gmail.com



determination of the structure-activity relationship has not been possible. Regarding cobalt complexes showing the activity, there are a few but neither their single crystal X-ray structures are known nor their turnover numbers are determined.18 Again, although a few dinuclear or oligonuclear compounds containing both Co^{III} and Co^{II} are known,^{19,20} the possibility of catecholase activity of those mixed-valence systems has not been checked. With the aim to explore catecholase activity by cobalt complexes, we have isolated three mixed-valence dinuclear Co^{III}Co^{II} complexes [Co^{III}Co^{II}L- $(N_3)_3$]·CH₃CN (1), $[Co^{III}Co^{II}L(OCN)_3]$ ·CH₃CN (2), and $[Co^{III}Co^{II}L$ - $(\mu$ -CH₃COO)₂](ClO₄) (3), derived from a tetraimino diphenolate macrocyclic ligand H_2L (Scheme 1), obtained on [2 + 2] condensation of 4-ethyl-2,6-diformylphenol and 2,2'-dimethyl-1,3diaminopropane.²¹ Herein, we report the syntheses, characterization, catecholase activity, and electrospray ionization mass spectroscopic (ESI-MS positive) study of these three complexes.

Experimental section

Caution! Azide and perchlorate complexes of metal ions are potentially explosive. Only a small amount of material should be prepared, and it should be handled with caution.

Materials and physical measurements

All the reagents and solvents were purchased from commercial sources and used as received. 4-Ethyl-2,6-diformylphenol was prepared according to the procedure reported for the synthesis of 4-ethyl-2,6-diformylphenol.²² Elemental (C, H, and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. IR spectra were recorded in the region 400–4000 cm⁻¹ on a Bruker-Optics Alpha-T spectrophotometer with samples as KBr disks. Electronic spectra were obtained by using a Shimadzu UV-3600 spectrophotometer. The electrospray ionization mass spectra were recorded on a Micromass Qtof YA 263 mass

spectrometer. The molar conductivity (Λ_M) of a 1 mM solution in DMF was measured at 25 °C with a Systronics conductivity bridge.

Syntheses

Synthesis of [Co^{III}Co^{II}L(N₃)₃]·CH₃CN (1). To a stirred acetonitrile solution (25 ml) of $[H_4L](ClO_4)_2$ (0.689 g, 1 mmol) were dropwise added successively an acetonitrile solution (15 ml) of $Co(ClO_4)_2 \cdot 6H_2O$ (0.732 g, 2 mmol) and an acetonitrile solution (5 ml) of triethylamine (0.404 g, 4 mmol). After 1 h, an aqueous solution (10 ml) of NaN₃ (0.260 g, 4 mmol) was added dropwise to the solution with stirring. Immediately, a reddish precipitate started to appear. After stirring for an additional 2 h, the mixture was heated to get almost a clear solution which was filtered to remove the suspended particles and the filtrate was kept at ambient temperature for slow evaporation. After a few days, a red crystalline compound containing diffraction quality crystals that deposited were collected by filtration, washed with an acetonitrile-water mixture and air dried. Yield: (0.53 g, 70%). Anal. calcd for C₃₂H₄₁N₁₄O₂Co₂: C, 49.81; H, 5.36; N, 25.41%. Found C, 49.77; H, 5.34; N, 25.46%. IR (KBr pellets, cm⁻¹): ν (N₃), 2055 s; ν (C=N), 1637. UV-vis (DMF) λ_{max} $(nm) [\varepsilon in M^{-1} cm^{-1}]: 380 (18\ 600), 581 (332), 1065 (16).$

[Co^{III}Co^{III}L(OCN)₃]·CH₃CN (2). This compound was prepared following the similar procedure as described above for 1, except using sodium cyanate instead of sodium azide. Yield: (0.57 g, 74%). Anal. calcd for C₃₅H₄₁N₈O₅Co₂: C, 54.48; H, 5.36; N, 14.52%. Found C, 54.44; H, 5.42; N, 14.57%. IR (KBr pellets, cm⁻¹): ν (OCN), 2211 s; ν (C=N), 1638. UV-vis (DMF) λ_{max} (nm) [ε in M⁻¹ cm⁻¹]: 376 (11 600), 581 (330), 1093 (10).

 $[Co^{III}Co^{II}L(\mu-CH_3COO)_2](ClO_4)$ (3). To a boiling methanol solution (30 ml) of 4-ethyl-2,6-diformylphenol (0.356 g, 2 mmol) were added successively a methanol solution (10 ml) of Co(ClO₄)·6H₂O (0.366 g, 1 mmol) and Co(OAc)₂·4H₂O (0.249 g, 1 mmol) and a methanol solution (20 ml) of 2,2'dimethyl-1,3-diaminopropane (0.208 g, 2 mmol). The resulting red solution was refluxed for one hour, after which it was concentrated to ca. 15 ml on a rotary evaporator. Then after filtration to remove any suspended particles, the filtrate was allowed to evaporate slowly at ambient temperature. After a few days, a red crystalline compound containing diffraction quality single crystals that deposited were collected by filtration, washed with cold methanol and air dried. Yield: (0.62 g, 75%). Anal. calcd for C₃₄H₄₄N₄O₁₀ClCo₂: C, 49.68; H, 5.40; N, 6.81%. Found C, 49.71; H, 5.37; N, 6.83%. IR (KBr pellets, cm⁻¹): ν (C=N), 1636; ν (CH₃COO), 1583 vs, 1441 s; ν (ClO₄), 1091 s, 623 w. UV-vis (DMF) λ_{max} (nm) [ε in M⁻¹ cm⁻¹]: 377 (11 200), 578 (329), 956 (10).

X-ray crystallography. The crystallographic data of the compounds **1–3** are summarized in Table 1. Intensity data of **1** and **2** were collected at 100 K and 296 K respectively, on a Bruker-APEX II SMART CCD diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) whereas intensity data

Paper

Compound	1	2	3	
Empirical formula	C ₃₂ H ₄₁ N ₁₄ O ₂ Co ₂	C ₃₅ H ₄₁ N ₈ O ₅ Co ₂	C ₃₄ H ₄₄ N ₄ O ₁₀ ClCo ₂	
Formula weight	771.64	771.63	822.07	
Crystal system	Monoclinic	Triclinic	Monoclinic	
Space group	C2/c	$P\bar{1}$	P2/c	
a (Å)	32.855(12)	9.631(4)	15.792(4)	
$b(\mathbf{\hat{A}})$	12.339(4)	12.255(5)	11.677(6)	
c (Å)	19.200(7)	16.296(7)	21.775(4)	
$\alpha(\circ)$	90.00	96.958(5)	90.00	
$\beta(\circ)$	113.975(5)	101.226(5)	104.040(10)	
γ (°)	90.00	104.979(5)	90.00	
$V(A^3)$	7112(4)	1792.4(14)	3895(2)	
Z	8	2	4	
D (calculated, g cm ⁻³)	1.441	1.430	1.402	
λ (Mo-K _{α}) (Å)	0.71073	0.71073	0.71073	
$\mu (mm^{-1})$	0.985	0.978	0.978	
$T(\mathbf{K})$	100(2)	296(2)	293(2)	
F(000)	3208	802	1708	
2θ range for data collection (°)	2.72-50.88	2.60-51.00	4.12-60.04	
Index ranges	$-39 \le h \le 39$	$-11 \le h \le 11$	$-22 \le h \le 22$	
C	$-14 \le k \le 14$	$-14 \le k \le 14$	$0 \le k \le 16$	
	$-23 \le l \le 23$	$-19 \le l \le 19$	$-30 \le l \le 30$	
No. of measured reflections	34 359	12 975	22 630	
No. of independent reflections	6533	6530	11 352	
R _{int}	0.0931	0.0238	0.1166	
No. of refined parameters	458	489	470	
No. of observed reflections, $I \ge 2\sigma(I)$	4421	4891	4726	
Goodness-of-fit on F^2 , S	1.016	1.022	0.980	
$R_1^a, WR_2^b [I \ge 2\sigma(I)]$	0.0520, 0.1282	0.0770, 0.2088	0.0502, 0.1228	
R_1^{a} , wR_2^{b} [all data]	0.0878, 0.1478	0.1014, 0.2300	0.1652, 0.1534	
Max., min. electron density (e $Å^{-3}$)	0.982, -0.647	2.305, -1.604	0.486, -0.391	
${}^{a}R_{1} = [\sum F_{o} - F_{c} / \sum F_{o}]. {}^{b}wR_{2} = [\sum w(F_{o})^{2} - $	$-F_{\rm c}^{2})^{2}/\sum w(F_{\rm o}^{2})^{2}]^{1/2}.$			

Downloaded by University of Toronto on 26 February 2013 Published on 03 January 2013 on http://pubs.rsc.org | doi:10.1039/C2DT32629A

of 3 were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K α radiation (λ 0.71073 Å) at 293 K. Data processing and absorption correction of 1 and 2 were done with the packages $SAINT^{23a}$ and SADABS^{23b} while a CAD4 Express Enraf-Nonius programs package and XCAD4 were used for data collection and reduction for 3. The structures were solved by direct and Fourier methods and refined by full-matrix least-squares based on F^2 using SHELXTL^{23c} and SHELXL-97^{23d} packages. During the development of the structures of 2 it became apparent that a few atoms were each disordered over two sites. These disordered atoms are Co2, N6, C32 and O4. This was allowed on refining freely and the final linked occupancy parameters for these disordered atoms are 0.85 and 0.15 for Co2, 0.85 and 0.15 for N6, and 0.80 and 0.20 for C32 and O4. While refining anisotropically, the U_{eq} values of O4 (occupancy 0.80) and O4A (occupancy 0.20) were 0.217 and 0.360, both are larger than usual in spite of splitting over two sites. As U_{eq} (anisotropic) of O4A was appreciably large, 0.36, this site was refined isotropically resulting in U_{eq} (isotropic) = 0.21. The U_{eq} value of C8 is also high, 0.262. However, no electron density around this atom was found and therefore splitting it over two disordered sites was not possible. Again, the largest residual electron density peak was 2.305 which is related to the heavy element Co1 in the structure. All these problems (larger U_{eq} or larger residual density peak) in the structure of 2 are related to poor quality of the crystal;²⁴ it has not been possible to isolate a

better quality crystal. During the development of structure 3 U_{eq} values of C8, O7 and O8 were found to be higher (>0.15). However it was only possible to split O7 over two sites, O7A $(U_{eq} = 0.167; \text{ occupancy} = 0.50)$ and O7B $(U_{eq} = 0.174; \text{ occupancy} = 0.50)$. No appreciable density was found around C8 and O8. It may be noted that thermal agitation of the methyl carbon atom (as C8) and the perchlorate oxygen atom (as O8) is not specific. All the hydrogen atoms in 1–3 were placed at geometrical positions with fixed thermal parameters. Except for O4A, all the nonhydrogen atoms were refined anisotropically, while O4A and all the hydrogen atoms were refined isotropically. The final least-squares refinements (R_1) based on $I > 2\sigma(I)$ converged to 0.0520, 0.0770 and 0.0502 for 1, 2 and 3, respectively.

Results and discussion

Syntheses, characterization and proposed composition in solution

The macrocyclic mixed-valence $\text{Co}^{III}\text{Co}^{II}$ azide/cyanate complexes $[\text{Co}^{III}\text{Co}^{II}\text{L}(N_3)_3]\cdot\text{CH}_3\text{CN}$ (1) and $[\text{Co}^{III}\text{Co}^{II}\text{L}-(\text{OCN})_3]\cdot\text{CH}_3\text{CN}$ (2) are readily obtained in high yield from the reaction of the perchlorate salt of diprotonated macrocyclic ligand $[\text{H}_4\text{L}](\text{ClO}_4)_2$, cobalt(II) perchlorate hexahydrate, triethylamine and NaN₃ (for 1) or NaNCO (for 2) in a 1:2:4:4 ratio. On the other hand, the mixed-valence bis(μ -acetate) $\text{Co}^{III}\text{Co}^{II}$

compound $[Co^{III}Co^{III}L(\mu-CH_3COO)_2](ClO_4)$ (3) was obtained in the template syntheses in which 4-ethyl-2,6-diformylphenol and 2,2'-dimethyl-1,3-diaminopropane (2 : 2) were allowed to condense in the presence of 1 equivalent of $Co(ClO_4)_2 \cdot 6H_2O$ and $Co(OAc)_2 \cdot 4H_2O$ (1 : 1). The elemental analyses clearly indicate a composition having Co^{III} and Co^{II} metal ions in each of 1–3.

The FT-IR spectra reveal the presence of C=N moieties in 1-3 (1636–1638 cm⁻¹), azide in 1 (2055 cm⁻¹), cyanate in 2 (2221 cm⁻¹), perchlorate in 3 (1091 and 622 cm⁻¹), and acetate in 3 (1583 and 1441 cm⁻¹). The difference in energy, 142 cm⁻¹, between the antisymmetric and symmetric carboxylate stretching frequencies in 3 is in line with the bidentate bridging mode.²⁵

The electronic spectra of the complexes were studied in DMF at ambient temperature. The complexes **1**–3 show an intense band at 380 nm (for **1**), 376 nm (for **2**), and 377 nm (for **3**) with an extinction coefficient (ε) in the range 11 200–18 600 M⁻¹ cm⁻¹ that can be assigned to the $\pi \rightarrow \pi^*$ transition associated with the azomethine group. All these three complexes exhibit one low-intensity ($\varepsilon = 16 \text{ M}^{-1} \text{ cm}^{-1}$ for **1** and 10 M⁻¹ cm⁻¹ for **2** and **3**) near-IR band (at 1065 cm⁻¹ for **1**, 1093 cm⁻¹ for **2**, and 956 cm⁻¹ for **3**) and a stronger band ($\varepsilon = 332 \text{ M}^{-1} \text{ cm}^{-1}$ for **1**, 330 M⁻¹ cm⁻¹ for **2**, and 329 M⁻¹ cm⁻¹ for **3**) at 581 nm, which are characteristic d–d bands for, respectively, high-spin Co^{II} and low-spin Co^{III} centers in valence-localized Co^{III}Co^{II} systems.²⁶ Thus, the spectral feature indicates that valences in **1**–3 are localized.

The molar conductance values at 298 K for 1–3 in different solvents are summarized in Table S1.[†] The nonelectrolytic nature of compounds 1 and 2 in the solid state is retained in solution as evidenced by the low molar conductivity values (2.9–40 ohm⁻¹ cm⁻¹ mol⁻¹ l). The 1:1 electrolytic nature of complexes 3 in the solid state is retained in solution as evidenced by their molar conductance values, 75 ohm⁻¹ cm⁻¹ mol⁻¹ l in DMF and 158 ohm⁻¹ cm⁻¹ mol⁻¹ l in acetonitrile.²⁷

Description of the structures of $[Co^{III}Co^{II}L(N_3)_3]$ ·CH₃CN (1), $[Co^{III}Co^{II}L(OCN)_3]$ ·CH₃CN (2) and $[Co^{III}Co^{II}L(\mu$ -CH₃COO)₂]-(ClO₄) (3)

The structures of compounds 1, 2, and 3 are shown in Fig. 1-3, respectively. The selected bond lengths and angles of 1, 2, and 3 are listed in Tables S2-S4 (ESI⁺), while selected bond lengths and angles and some other structural parameters of the three complexes are compared in Table 2. The structures show that all the three compounds are dicobalt systems derived from tetraiminodiphenolate macrocyclic ligand L²⁻. While 1 and 2 are diphenoxo-bridged, 3 is a heterobridged bis(µ-phenoxo)bis- $(\mu$ -acetate) system. In addition to the dinegative organic ligand, L^{2–}, the presence of three mononegative moieties (three azides in 1, three cyanates in 2 and two acetates and one perchlorate in 3) in the composition of all the three complexes indicates that all of 1-3 are Co^{III}Co^{II} systems. As described below, the relative bond lengths involving the two metal centers indicate that the Co1 center is in the +III state while the Co2 center is in the +II state. Each of the two $N(imine)_2O(phenoxo)_2$



Fig. 1 Crystal structure of $[Co^{III}Co^{II}L(N_3)_3]$ -CH₃CN (1). All the hydrogen atoms and the solvated acetonitrile molecule are omitted for clarity.



Fig. 2 Crystal structure of $[Co^{III}CO^{II}CO^{II}CO(N)_3]$ -CH₃CN (**2**). All the hydrogen atoms and the solvated acetonitrile molecule are omitted for clarity. Of the two disordered positions of one cobalt, nitrogen, carbon and oxygen atom of the coordinated cyanate molecule, the one with high occupancy is shown here.

compartments of L^{2-} satisfy four coordination positions and provide the basal plane for each of the two metal ions in 1–3. In 1 and 2, the Co^{III} center (Co1) is hexacoordinated and adopts a distorted octahedral environment in which the two axial positions are occupied by the nitrogen atoms of two azide (in 1) or two cyanate (in 2) ligands, while the Co^{II} center (Co2) is pentacoordinated and adopts a distorted square pyramidal environment in which the axial position is occupied by the nitrogen atom of an azide (in 1) or a cyanate (in 2) ligand. On the other hand, both the Co^{III} (Co1) and Co^{II} (Co2) centers in 3 are hexacoordinated and adopt a distorted octahedral geometry in which the axial positions are occupied by the oxygen



Fig. 3 Crystal structure of $[Co^{III}Co^{II}L(\mu-CH_3COO)_2](CIO_4)$ (3). All the hydrogen atoms and the perchlorate ion are omitted for clarity.

atoms of two $\mu_{1,3}$ -acetate ligands. From the least-squares N₂O₂ basal plane, while the displacement of the hexacoordinated metal ions in 1-3 is small (<0.16), the pentacoordinated metal centers (Co2) in 1 and 2 are shifted significantly (by 0.55 and 0.60, respectively) towards the apical azide or cyanate nitrogen atom. As compared in Table 2, the cobalt-O(phenoxo) and cobalt-N(imine) bond distances in all the three complexes and the cobalt-O(acetate) bond distances in 3 involving Co1 are significantly shorter than the corresponding bond lengths involving Co2, indicating that Co1 is the Co^{III} center while Co2 is the Co^{II} center. On the other hand, the cobalt(III)-N(azide) and $cobalt(\pi)$ -N(azide) distances in 1 are almost identical, as are the cobalt(III)-N(cyanate) and cobalt(II)-N(cyanate) distances in 2, which is due to the shifting of the cobalt(II) center towards the apical atom. In all of 1-3, the cisoid angles for the Co^{III} centers (overall range for $1-3 = 80.38(16)-95.4(2)^{\circ}$) are less deviated than for the Co^{II} centers (overall range for 1-3 = 74.97(15)-122.4(2)°). Transoid angles for the Co^{III} and Co^{II} centers are more significantly different; the overall range for the Co^{III} centers in **1-3** is 171.82(19)–178.7(3)°, the range for the Co^{II} center in 3 is 151.86(9)–169.60(10)°, and the overall range for the Co^{II} centers in **1** and **2** is 139.91(9)–150.01(12)°. The metal…metal separation (3.064 Å in 1, 3.067 Å in 2, 2.856 Å in 3) and the Co-O(phenoxo)-Co bridge angles (99.74(12)° and 100.82(12)° in 1, 99.36(17)° and 101.20(17)° in 2, 92.77(8)° and 92.87(8)° in 3) are comparable with each other and also with previously reported similar macrocyclic dicopper(II) systems. The macrocyclic ligand in 1-3 adopts a puckered configuration as evidenced from the dihedral angle between the two aromatic rings, 69.96°, 58.04° and 65.70°, respectively. We have also performed the bond valence sum (BVS) calculations²⁸ to assign the oxidation states of the two cobalt centers.^{20a-c} The BVS values of 3.72/4.36/3.44 and 2.31/2.34/2.40 for the Co1 and Co2 centers, respectively, in complexes 1-3 corroborate the assignment on the basis of bond lengths. However, it is not clear why the Co^{III} (Co1) center in 1 and 2 has such a high BVS value (3.72/4.36) but there is no evidence to suggest it as a Co^{IV} center. It may be mentioned as well that such a high value of the Co^{III} center in mixed-valence systems is not unknown.^{20c}

Compound	Metal center	Co– phenoxo	Co-imine	Co-azide	Co-cyanate	Co-acetate	Cisoid angles	Transoid angles	$d_{\rm N,O}$	d_{M}	M–O (phenoxo)–M	М…М
1	Co1 (Co ^{III}) Co2 (Co ^{II})	1.929(3), 1.933(3) 2.042(3), 2.076(3)	1.911(3), 1.915(3) 2.039(4), 2.059(3)	1.947(4), 1.969(3) 1.978(4)	_	_	81.41(11)- 95.27(14) 75.39(10)- 113.05(15)	172.89(13)- 178.30(15) 145.53(12)- 150.01(12)	0.008 0.036	0.004 0.551	99.74(12), 100.82(12)	3.064
2	Co1 (Co ^{III}) Co2 (Co ^{II})	1.930(4), 1.945(4) 2.036(4), 2.074(4)	1.910(5), 1.919(5) 2.055(5), 2.068(5)	_	1.700(12), 1.945(6) 1.950(7)	_	80.38(16)- 95.4(2) 74.97(15)- 122.4(2)	171.82(19)- 178.7(3) 139.91(19)- 149.34(19)	0.022 0.093	0.011 0.604	99.36(17), 101.20(17)	3.067
3	$\begin{array}{l} \text{Co1} \left(\text{Co}^{\text{III}} \right) \\ \text{Co2} \left(\text{Co}^{\text{II}} \right) \end{array}$	1.922(2), 1.923(2) 2.018(2), 2.020(2)	1.931(3), 1.934(3) 2.016(3), 2.017(3)	_	_ _	1.909(2), 1.933(2) 2.100(3), 2.279(2)	87.25(9)- 94.72(12) 77.82(9)- 107.39(12)	176.18(10) - 177.85(10) 151.86(9) - 169.60(10)	0.006 0.007	0.001 0.156	92.77(8), 92.87(8)	2.856

Catecholase activity

3,5-Di-*tert*-butylcatechol (3,5-DTBCH₂) is usually used to study the catecholase activity for the model complexes because of the ease of oxidation of 3,5-DTBCH₂ to its corresponding quinone, 3,5-di-*tert*-butylquinone (3,5-DTBQ), the latter of which has a characteristic transition at *ca.* 400 nm. To check the ability of complexes 1–3 to behave as a catalyst for catecholase activity, a 0.25×10^{-4} (M) solution of a complex was treated with a 100-fold concentrated solution of 3,5-DTBCH₂ and the course of the reaction was followed by recording UVvis spectra of the mixture under aerobic condition times up to 30 or 120 min. Experiments for complex 1 were done in three solvents, methanol, acetonitrile, and DMF, while those for 2 and 3 were done in acetonitrile and DMF because the latter two compounds are practically insoluble in methanol.

Spectral changes of complex 1 in acetonitrile are shown in Fig. 4. Because of the addition of 3,5-DTBH₂, the band of 1 at 380 nm becomes slightly red shifted to 400 nm with a gradual increase of intensity, indicating more and more formation of the quinone, 3,5-DTBQ. Clearly, complex 1 in acetonitrile shows catecholase activity. Similar spectral changes take place for complex 1 in methanol (Fig. S1, ESI⁺). On the other hand, generation of the quinone band does not take place for complex 1 in DMF and also for 2 and 3 in acetonitrile and DMF, which clearly indicates that complexes 2 and 3 are not catalysts of catecholase activity and complex 1 is not a catalyst in DMF. Kinetic studies of the catecholase activity of complex 1 have been performed to understand the extent of its efficiency. For this purpose, a 0.25×10^{-4} (M) solution of a complex was treated with the substrate solution having concentration ranging between 10-fold and 100-fold greater than that of the complex. The experiments were done at a constant temperature, 25 °C, under aerobic condition. For a particular complex-substrate mixture, a time scan at the maximum of



Fig. 4 The spectral profile showing the increase of the quinone band at 400 nm after the addition of 100-fold of 3,5-DTBCH₂ to a solution containing complex $[Co^{III}Co^{III}L(N_3)_3]$ -CH₃CN (**1**) (0.25 × 10⁻⁴ M) in MeCN. The spectra were recorded after each 5 min.



Fig. 5 Initial rates *versus* substrate concentration for the 3,5-DTBCH₂ \rightarrow 3,5-DTBQ oxidation reaction catalyzed by complex [Co^{III}CO^{III}C(N₃)₃]-CH₃CN (**1**) in acetonitrile. The inset shows the Lineweaver–Burk plot. Symbols and solid lines represent the observed and simulated profiles, respectively.

the quinone band was carried out for a period of 30 minutes in acetonitrile and 120 minutes in methanol. It may be noted here that blank experiments in both for acetonitrile and methanol without the catalyst do not show formation of the quinone up to 6 hours. The rate constant for a particular complex-substrate mixture was determined from the optical density versus time plot by the initial rate method. The rate constant versus concentration of substrate data were then analyzed on the basis of the Michaelis-Menten approach of enzymatic kinetics to get the Lineweaver-Burk plot as well as the values of the parameters V_{max} , K_{M} , and K_{cat} . The observed and simulated rate constant versus [substrate] plot and the Lineweaver-Burk plot for complex 1 in acetonitrile are shown in Fig. 5 while similar plots for complex 1 in methanol are shown in Fig. S2 (ESI⁺). The kinetic parameters are listed in Table 3. The turnover number (K_{cat}) for complex **1** is 482.16 h⁻¹ in acetonitrile and 45.38 h⁻¹ in methanol. These values lie in the range of the K_{cat} values of the di- or oligonuclear copper(II) systems⁷⁻¹⁵ behaving as functional models of catechol oxidase. Therefore the Co^{III}Co^{II} compound 1 can also be considered as a functional model of catechol oxidase.

Electrospray ionization mass spectral study

The electrospray ionization mass spectra (ESI-MS positive) of acetonitrile solutions of compounds 1–3 were recorded and are shown in Fig. 6, S3 and S4 (ESI[†]), respectively. Compound 1 exhibits three peaks at m/z = 688 (52%, line to line separation 1.0), 753 (31%, line to line separation 1.0), and 302 (12%, line to line separation 0.5). The peaks at m/z = 688 and 753 are assignable to $[Co^{II}Co^{II}L(N_3)_2]^+$ ($C_{30}H_{38}N_{10}O_2CO_2$) and $[Co^{II-1}Co^{II}L(N_3)_3Na]^+$ ($C_{30}H_{38}N_{13}O_2NaCO_2$), respectively, while the low intensity peak at 302 arises due to the reduced species $[Co^{II}Co^{II}L]^{2+}$ ($C_{30}H_{38}N_4O_2CO_2$). Compound 2 exhibits only one peak at m/z = 688 (64%, line to line separation 1.0), which is assignable to $[Co^{III}Co^{II}L(OCN)_2]^+$ ($C_{32}H_{38}N_6O_4CO_2$). Compound 3 exhibits three peaks at m/z = 663 (11%, line to line separation 1.0), 331 (18%, line to line separation 0.5), and 302 (58%, line

 $\label{eq:complex} \mbox{Table 3} \quad \mbox{Kinetic parameters for the complex } [Co^{II}Co^{II}L(N_3)_3] \cdot CH_3 CN \mbox{(1)}$

Complex	Solvent	V_{\max} (M min ⁻¹)	Std. error	$K_{\mathbf{M}}\left(\mathbf{M}\right)$	Std. error	$K_{\rm cat} \left({{{\rm{h}}^{-1}}} \right)$
1	MeCN MeOH	2.009×10^{-4} 1.891×10^{-5}	$5.15 \times 10^{-5} \\ 4.168 \times 10^{-6}$	0.003011 0.001576	0.001227 0.0007015	482.16 45.38



Fig. 6 Electrospray mass spectrum (ESI-MS positive) of $[Co^{III}CO^{II}CO^{II}CN_3)_3]$ -CH₃CN (1) in acetonitrile showing observed and simulated isotopic distribution patterns.



Fig. 7 Electrospray mass spectrum (ESI-MS positive) of a 1:100 mixture of $[Co^{III}Co^{II}L(N_3)_3]$ -CH₃CN (1) and 3,5-DTBCH₂ in acetonitrile, recorded after 15 minutes of mixing. Both the observed and simulated isotopic distribution patterns are shown.

to line separation 0.5). The peaks at m/z = 331 are assignable to $[Co^{III}Co^{II}L(\mu-CH_3COO)]^{2+}$ ($C_{32}H_{41}N_4O_4Co_2$), while the remaining two peaks at 302 and 663 arise due to the two reduced species $[Co^{II}Co^{II}L]^{2+}$ ($C_{30}H_{38}N_4O_2Co_2$) and $[Co^{II}Co^{II}L-(\mu-CH_3COO)]^+$ ($C_{32}H_{41}N_4O_4Co_2$), respectively. As shown in Fig. 6, S3 and S4 (ESI[†]), the isotopic distributions of the observed and the simulated spectral patterns are in excellent agreement with each other, indicating right assignment of the positive ions.

To get an insight into the nature of possible complexsubstrate intermediates, ESI-MS positive spectra of a 1:100 mixture of complex 1 and 3,5-DTBCH₂ were recorded after 15 minutes of mixing in acetonitrile. The observed and simulated patterns are presented in Fig. 7. In this case, four peaks are observed at m/z = 243 (99%, line to line separation 1.0), 463 (12%, line to line separation 1), 889 (21%, line to line separation 1.0), and 910 (26%, line to line separation 1.0). The peaks at m/z = 243 and 463 correspond, respectively, to the quinone–sodium aggregates $[(3,5-DTBQ)Na]^+$ ($C_{14}H_{20}O_2Na)$ and $[(3,5-DTBQ)_2Na]^+$ ($C_{28}H_{40}O_4Na$). The remaining peaks at m/z = 889 and 910 are quite interesting because the peak position and matching of the isotopic distribution of the observed and the simulated patterns clearly indicate that these peaks arise due to 1:1 complex–substrate aggregates $[CO^{II}_{2}L(\mu-3,5-DTBC^{2-})Na]^+$ ($C_{44}H_{58}N_7O_4NaCo_2$) and $[CO^{III}CO^{II}_{2}L(N_3)_2(3,5 DTBCH^-)H]^+$ ($C_{44}H_{60}N_{10}O_4Co_2$). It is logical to consider the monoanionic 3,5-DTBCH⁻ species in $[CO^{III}CO^{II}_{2}L(N_3)_2(3,5 DTBCH^-)H]^+$ as coordinated in monodentate mode through the phenolate oxygen atom to the cobalt(III) center and the dianionic 3,5-DTBC²⁻ species in $[CO^{II}_{2}L(\mu-3,5-DTBC^{2-})Na]^+$ as a bridging ligand through the two phenolate oxygen atoms to the two cobalt(II) centers.

Comparison with the previous related studies: significant aspects

To understand why a metal compound is an active catalyst while another closely related compound is not, determination of single crystal X-ray structures of the compounds is very much important. Again, determination of turnover number (K_{cat}) of the catalysts is important to understand their relative efficiency. In addition, a sufficient number of active catalysts having closely similar composition/structure is required in order to frame a structure-property or structure-efficiency correlation. Such criteria are fulfilled for several series of dicopper(II) compounds as the active catalyst of catechol oxidase activity and therefore a few structure-efficiency correlations have been proposed in which efficiency is the function of metal---metal distance, coordination geometry around the metal center, nature of the exogenous bridging ligand, flexibility of the primary ligand etc.^{6,7,12,13} However, the literature survey reveals that the problem is rather complicated because a correlation is applicable for only a set of a few compounds; straightforward correlation even in dicopper(II) compounds is still lacking. On the other hand, studies of catechol oxidase activity by complexes of metal ions, other than copper(II), are very much less and therefore no correlation has yet been proposed.

Regarding complexes of metal ions of cobalt as an active catalyst for catechol oxidase activity, a few examples are known. To the best of our knowledge, these include one mononuclear Co^{II} , 18a,b four dinuclear $\text{Co}^{II}\text{Co}^{II}$, 18c and two dinuclear $\text{Co}^{III}\text{Co}^{III}$ compounds. 18c However, single crystal X-ray structures of none of these have been determined. Moreover, kinetic studies to determine K_{cat} values of none of these have been carried out. So, compound **1** in the present investigation is the sole example of a cobalt containing catalyst of catecholase activity for which both the single crystal X-ray structure and K_{cat} values have been determined.

As already mentioned, while $[Co^{III}Co^{II}L(N_3)_3]$ ·CH₃CN (1) is a catalyst, [Co^{III}Co^{III}L(OCN)₃]·CH₃CN (2) and [Co^{III}Co^{III}L(µ-OAc)₂]- (ClO_4) (3) are inactive regarding catecholase activity. Although catecholase activity is a property in solution, the activity or inactivity as well as the relative extent of activity are usually explained in terms of solid state structures.^{6a,b,7,8,11,12} Moreover, as mentioned above, the electrolytic nature in solution and in solid state of 1-3 are the same, indicating that the bridging core along with the ligand environment of 1-3 in solid state and in solution are most probably the same. Therefore, it is logical to address activity/inactivity of 1-3 in terms of their crystal structures. The inactivity of 3 is probably due to its triple bridged composite structure, which prevents the attack of the catechol moiety on the metal center(s). On the other hand, as 1 and 2 have similar types of structures, it looks surprising, at least apparently, why 1 is active but 2 is inactive. However, while the two cobalt(III)-N(azide) distances in 1 are almost similar, 1.947(4) and 1.969(3) Å, the two cobalt(III)-N(cyanate) distances in 2 are significantly different, 1.700(12) and 1.945(6) Å. The more tightly bound cyanate of cobalt(III) and the coordinated cyanate of cobalt(II) lie at the same side, both of which are to be eliminated for providing space of the dideprotonated, dinegative, and bridging catechol moiety. But, elimination of the tightly bound cyanate is rather difficult, which is probably the reason for inactivity of complex 2.

Whatever the aftermath, coordination of the catechol moiety to the metal center is an essential requirement for a complex to show catecholase activity. In the two proposed mechanisms regarding the in vivo cycle, 1:1 adduct formation between a dicopper(II) core and the substrate has been mentioned. While monodentate asymmetric coordination of the substrate has been proposed in one mechanism (Krebs's mechanism),^{6f,g} simultaneous coordination of the substrate to both copper centers in the dinucleating bridging fashion is suggested in the second (Solomon's mechanism).^{6d} Although complex 1 is not a Cu^{II}Cu^{II} but a Co^{III}Co^{II} system, two 1:1 complex substrate aggregates [Co^{III}Co^{II}L(N₃)₂(3,5-DTBCH⁻)H]⁺ and [Co^{II}₂L(µ-3,5-DTBC²⁻)Na]⁺ having a monodentate (as in one mechanism) catechol moiety in the first aggregate and a bridging bidentate (as in the second mechanism) catechol moiety in the second aggregate have been identified in the ESI-MS positive spectrum of the present investigation. We should keep in mind that the complex-substrate aggregate identified in the ESI-MS spectrum may not be a real intermediate in the catalytic cycle because such aggregates may be formed in situ because of the relative stability when compared to the other cationic species in the time scale of the ESI-MS spectrum. Similar should be the case for the complex-substrate aggregates identified in the solid state, where the solid state effects may enforce the stability. Nonetheless, the aggregates identified here in the ESI-MS positive spectrum deserve importance because they indicate clear evidence of the coordination and bridging ability of the substrate to the complexes. Moreover, the species mimic the species proposed in two mechanisms at least in terms of stoichiometry (1:1) and coordination mode (monodentate in one and bridging in another).

Conclusions

The present study demonstrates first structurally characterized mixed-valence dinuclear cobalt complexes to check their catechol oxidase activity. Interestingly, [Co^{III}Co^{III}L(N₃)₃]·CH₃CN (1) is the unique example of (i) a structurally characterized complex showing catecholase activity, (ii) a cobalt complex for which turnover number has been determined, and (iii) a mixed valence Co^{III}Co^{II} complex showing catecholase activity. In the ESI-MS positive spectra, two complex-substrate aggregates have been identified which contain, respectively, a monodentate catechol moiety and a bidentate bridging catechol moiety and thus these species mimic, interestingly, the proposed intermediates in the mechanism of in vivo cycles of the native dicopper enzyme. Due to the availability of structure and activity/ K_{cat} data in cobalt systems here only, the probable reason for activity/inactivity of the three title compounds has been explained. The exploration of both structure and activity/ K_{cat} of more cobalt systems in general and $\text{Co}^{\text{III}}\text{Co}^{\text{II}}$ complexes in particular will be important for further enlightenment of the intimate reason for activity/inactivity and framing structure-activity correlations, which are to date lacking in systems having metal ions other than $copper(\pi)$.

Acknowledgements

Financial support from the Government of India through the Department of Science and Technology (Project No. SR/S1/ IC-42/2011) and the Council for Scientific and Industrial Research (CSIR Fellowship to S. Mondal) is gratefully acknowledged. Crystallography of **1** and **2** was performed at the DST-FIST, India-funded Single Crystal Diffractometer Facility at the Department of Chemistry, University of Calcutta. P. L. thanks Université Paris Descartes, Laboratoire de Cristallographie et RMN biologiques UMR 8015, Faculté de Pharmacie for single crystal X-ray data collection of **3**.

Notes and references

- 1 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.
- 2 (a) G. C. Allen and N. S. Hush, Prog. Inorg. Chem., 1967, 8, 357; (b) N. S. Hush, Prog. Inorg. Chem., 1967, 8, 391.
- 3 G. Blondin and J.-J. Girerd, Chem. Rev., 1990, 90, 1359.
- 4 (a) W. Kaim and G. K. Lahiri, Angew. Chem., Int. Ed., 2007,
 46, 1778; (b) K. D. Demadis, C. M. Hartshorn and T. J. Meyer, Chem. Rev., 2001, 101, 2655; (c) W. Kaim, A. Klein and M. Glöckle, Acc. Chem. Res., 2000, 33, 755; (d) D. M. D'Alessandro and F. R. Keene, Chem. Rev., 2006, 106, 2270; (e) D. M. D'Alessandro and F. R. Keene, Chem. Soc. Rev., 2006, 35, 424; (f) B. S. Brunschwig, C. Creutz and N. Sutin, Chem. Soc. Rev., 2002, 31, 168.
- 5 (a) D. M. D'Alessandro and F. R. Keene, *Chem. Rev.*, 2006, 106, 2270; (b) S. Hazra, S. Sasmal, M. Fleck, F. Grandjean,

M. T. Sougrati, M. Ghosh, T. D. Harris, P. Bonville, G. J. Long and S. Mohanta, *J. Chem. Phys.*, 2011, 134, 174507; (c) S. K. Dutta, J. Ensling, R. Werner, U. Flörke, W. Haase, P. Gütlich and K. Nag, *Angew. Chem., Int. Ed. Engl.*, 1997, 36, 834; (d) S. Drueke, P. Chaudhuri, K. Pohl, K. Wieghardt, X.-Q. Ding, E. Bill, A. Sawaryn, A. X. Trautwein, H. Winkler and S. J. Gurman, *J. Chem. Soc., Chem. Commun.*, 1989, 59.

- 6 (a) I. A. Koval, P. Gamez, C. Belle, K. Selmeczi and J. Reedijk, *Chem. Soc. Rev.*, 2006, 35, 814; (b) K. Selmeczi, M. Reglier, M. Giorgi and G. Speier, *Coord. Chem. Rev.*, 2003, 245, 191; (c) R. Than, A. A. Feldmann and B. Krebs, *Coord. Chem. Rev.*, 1999, 182, 211; (d) E. I. Solomon, U. M. Sundaram and T. E. Machonkin, *Chem. Rev.*, 1996, 96, 2563; (e) N. Kitajima and Y. Moro-oka, *Chem. Rev.*, 1994, 94, 737; (f) T. Klabunde, C. Eicken, J. C. Sacchettini and B. Krebs, *Nat. Struct. Biol.*, 1998, 5, 1084; (g) C. Eicken, B. Krebs and J. C. Sacchettini, *Curr. Opin. Struct. Biol.*, 1999, 9, 677.
- 7 (a) J. Reim and B. Krebs, J. Chem. Soc., Dalton Trans., 1997, 3793; (b) N. A. Rey, A. Neves, A. J. Bortoluzzi, C. T. Pich and H. Terenzi, Inorg. Chem., 2007, 46, 348; (c) C. Belle, C. Beguin, I. Gautier-Luneau, S. Hamman, C. Philouze, J. L. Pierre, F. Thomas and S. Torelli, Inorg. Chem., 2002, 41, 479; (d) J. Anekwea, A. Hammerschmidta, A. Rompelb and B. Krebs, Z. Anorg. Allg. Chem., 2006, 632, 1057; (e) J. Ackermann, F. Meyer, E. Kaifer and H. Pritzkow, Chem.-Eur. J., 2002, 8, 247; (f) J. Mukherjee and R. Mukherjee, Inorg. Chim. Acta, 2002, 337, 429; (g) D. Ghosh, T. K. Lal, S. Ghosh and R. Mukherjee, Chem. Commun., 1996, 13; (h) D. Ghosh and R. Mukherjee, Inorg. Chem., 1998, 37, 6597.
- 8 (a) M. Merkel, N. Mçller, M. Piacenza, S. Grimme, A. Rompel and B. Krebs, *Chem.-Eur. J.*, 2005, 11, 1201;
 (b) C. Fernandes, A. Neves, J. Bortoluzzi, A. S. Mangrich, E. Rentschler, B. Szpoganicz and E. Schwingel, *Inorg. Chim. Acta*, 2001, 320, 12;
 (c) A. Neves, L. M. Rossi, A. J. Bortoluzzi, A. S. Mangrich, W. Haase and R. Werner, *J. Braz. Chem. Soc.*, 2001, 12, 747.
- 9 P. K. Nanda, V. Bertolasi, G. Aromí and D. Ray, *Polyhedron*, 2009, **28**, 987.
- 10 R. Gupta, S. Mukherjee and R. Mukherjee, *Polyhedron*, 2000, **19**, 1429.
- 11 (a) S. Majumder, S. Sarkar, S. Sasmal, E. C. Sañudo and S. Mohanta, *Inorg. Chem.*, 2011, 50, 7540; (b) S. Sarkar, S. Majumder, S. Sasmal, L. Carrella, E. Rentschler and S. Mohanta, *Polyhedron*, 2013, 50, 270.
- 12 C.-H. Kao, H.-H. Wei, Y.-H. Liu, G.-H. Lee, Y. Wang and C.-J. Lee, *J. Inorg. Biochem.*, 2001, **84**, 171.
- M. Thirumavalavan, P. Akilan, M. Kandaswamy, G. Chinnakali, G. Senthil Kumar and H. K. Fun, *Inorg. Chem.*, 2003, 42, 3308.
- 14 S. J. Smith, C. J. Noble, R. C. Palmer, G. R. Hanson, G. Schenk, L. R. Gahan and M. Riley, *J. Biol. Inorg. Chem.*, 2008, 13, 499.
- 15 J. Manzur, A. M. García, A. Vega and A. Ibañez, *Polyhedron*, 2007, **26**, 115.

- 16 (a) S. Mukherjee, T. Weyhermüller, E. Bothe, K. Wieghardt and Ρ. Chaudhuri, Dalton Trans., 2004, 3842. (b) A. Majumder, S. Goswami, S. R. Batten, M. S. E. Fallah, J. Ribas and S. Mitra, Inorg. Chim. Acta, 2006, 359, 2375; (c) G. Blay, I. Fernández, J. R. Pedro, R. Ruiz-García, T. Temporal-Sánchez, E. Pardo, F. Lloret and M. C. Muñoz, J. Mol. Catal. A: Chem., 2006, 250, 20; (d) M. U. Triller, D. Pursche, W.-Y. Hsieh, V. L. Pecoraro, A. Rompel and B. Krebs, Inorg. Chem., 2003, 42, 6274; (e) I. Cs. Szigyártó, L. I. Simándi, L. Párkányi, L. Korecz and G. Schlosser, Inorg. Chem., 2006, 45, 7480; (f) J. Kaizer, R. Csonka, G. Baráth and G. Speier, Transition Met. Chem., 2007, 32, 1047.
- 17 (a) T. L. Simándi and L. I. Simándi, J. Chem. Soc., Dalton Trans., 1999, 4529; (b) L. I. Simándi and T. L. Simándi, J. Inorg. Biochem., 2001, 86, 332.
- 18 (a) T. L. Simándi and L. I. Simándi, *React. Kinet. Catal.* Lett., 1998, 65, 301; (b) L. I. Simándi and T. L. Simándi, J. Chem. Soc., Dalton Trans., 1998, 3275; (c) C. R. K. Rao and P. S. Zacharias, *Polyhedron*, 1997, 16, 1201.
- 19 (a) B. F. Hoskins and G. A. Williams, Aust. J. Chem., 1975, 28, 2593; (b) F. Hoskins, R. Robson and G. A. Williams, Inorg. Chim. Acta, 1976, 16, 121.
- 20 (a) S. Banerjee, M. Nandy, S. Sen, S. Mandal, G. M. Rosair, A. M. Z. Slawin, C. J. G. García, J. M. Clemente-Juan, E. Zangrando, N. Guidolin and S. Mitra, *Dalton Trans.*, 2011, 1652; (b) S. S. Tandon, S. D. Bunge, R. Rakosi, Z. Xu and L. K. Thompson, *Dalton Trans.*, 2009, 6536; (c) T. S. M. Abedin, L. K. Thompson and D. O. Miller, *Chem. Commun.*, 2005, 5512; (d) I. C. Lazzarini, L. Carrella, E. Rentschler and P. Alborés, *Polyhedron*, 2012, **31**, 779.
- 21 S. Majumder, M. Fleck, C. R. Lucas and S. Mohanta, *J. Mol. Struct.*, 2012, **1020**, 127.
- 22 F. Ullman and K. Brittner, Chem. Ber., 1909, 42, 2539.
- 23 (a) Bruker-Nonius, APEX-II, SAINT-Plus and TWINABS, Bruker-Nonius AXS Inc., Madison, Wisconsin, USA, 2004;
 (b) G. M. Sheldrick, SAINT (Version 6.02), SADABS (Version 2.03), Bruker AXS Inc., Madison, Wisconsin, 2002;
 (c) SHELXTL (version 6.10), Bruker AXS Inc., Madison, Wisconsin, 2002; (d) G. M. Sheldrick, SHELXL-97, Crystal Structure Refinement Program, University of Göttingen, 1997.
- 24 S. Mandal, J. Mukherjee, F. Lloret and R. Mukherjee, *Inorg. Chem.*, 2012, **51**, 13148.
- 25 (a) K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley, New York, 3rd edn, 1978; (b) G. Socrates, Infrared Characteristic Group Frequencies, Wiley, New York, 1980; (c) S. K. Dutta, R. Werner, U. Flörke, S. Mohanta, K. K. Nanda, W. Haase and K. Nag, Inorg. Chem., 1996, 35, 2292.
- 26 P. Chaudhuri, J. Querbach, K. Wieghardt, B. Nuber and J. Weiss, J. Chem. Soc., Dalton Trans., 1990, 271.
- 27 W. J. Geary, Chem. Rev., 1971, 7, 81.
- 28 (a) N. E. Brese and M. O'Keeffe, Acta Crystallogr., Sect. B: Struct. Sci., 1991, 47, 192; (b) I. D. Brown and D. Altermatt, Acta Crystallogr., Sect. B: Struct. Sci., 1985, 41, 244; (c) H. H. Thorp, Inorg. Chem., 1992, 31, 1585; (d) G. J. Palenik, Inorg. Chem., 1997, 36, 122.