Synthesis, spectral characterization, and structural investigation of mononuclear salen-type Cu(II) and Zn(II) complexes of a potentially octadentate N_2O_6 Schiff base ligand derived from binaphthol

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Received: 19 February 2013/Accepted: 6 May 2013/Published online: 7 June 2013 © Springer Science+Business Media Dordrecht 2013

Abstract A new potentially octadentate N_2O_6 Schiff base ligand, H_2L derived from the condensation of 2,2'-(1,1'binaphthyl-2,2'-diylbis(oxy))dianiline and o-vanillin, along with its copper(II) and zinc(II) complexes, is synthesized and has been characterized by elemental analyses, IR, UVvis, ¹H and ¹³C NMR spectra, as well as conductivity measurements. H_2L forms mononuclear complexes of 1:1 (metal:ligand) stoichiometry with Cu(II) and Zn(II), and conductivity data confirm the non-electrolyte nature of these complexes. The [ZnL] and [CuL] complexes display very different solid-state structures, as determined by X-ray crystallography. While the [ZnL] complex has a distorted octahedral geometry about the metal, the [CuL] complex displays a distorted square planar geometry about the copper, with long Cu–O(ether) distances of 2.667 Å.

Introduction

Schiff base ligands play an important role in inorganic chemistry as they form stable complexes with most transition

Electronic supplementary material The online version of this article (doi:10.1007/s11243-013-9728-2) contains supplementary material, which is available to authorized users.

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A. G. Blackman · S. A. Cameron Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand metals in a variety of oxidation states [1-5]. Among such ligands, tetradentate salen, derived from the condensation of two equivalents of salicylaldehyde with one equivalent of ethylenediamine [17], has been of particular importance in coordination chemistry, especially in homogeneous transition metal-mediated catalysis [6-16]. Transition metal complexes of salen have been known since at least 1931 [17–20], but extensive investigations have been carried out in the years since chiral variants were first applied to asymmetric catalysis in the early 1990s [21, 22]. Modified salen complexes have served as catalysts in a variety of reactions such as asymmetric epoxidation [7], copolymerization of carbon dioxide with epoxides [10, 11], and hydrolytic kinetic resolution of racemic epoxides [23, 24], depending on the metal employed. In the present work, we report the synthesis and characterization of a new salen-derived ligand, H₂L, containing 8 potential donor atoms. The X-ray structures of the Cu(II) and Zn(II) complexes of this ligand are reported; somewhat surprisingly, the two complexes display very different geometries about the metal centers.

Experimental

Materials and measurements

2,2'-(1,1'-Binaphthyl-2,2'-diylbis(oxy))dianiline was synthesized according to the literature procedure [25–29]. Solvents, 1,1'-binaphthyl-2,2'-diol, o-vanillin, 1-fluoro-2-nitrobenzene, and metal salts were purchased from Merck and used without further purification.

Infrared spectra were collected using KBr pellets on a BIO-RAD FTS-40A spectrophotometer $(4,000-400 \text{ cm}^{-1})$. A Perkin-Elmer Lambda 45 (UV–Vis) spectrophotometer was used to record the electronic spectra. CHN analyses

Table 1 Crystal data and structure refinement for [ZnL]·CH₃CN and [CuL]·2CHCl₃ complexes

Empirical formula	C ₅₀ H ₃₇ N ₃ O ₆ Zn	C ₅₀ H ₃₆ Cl ₆ CuN ₂ O ₆	
Formula weight	841.20	1037.05	
Temperature	89(2) K	89(2) K	
Wavelength (Å)	0.71069	0.71073	
Crystal system	Monoclinic	Monoclinic	
Space group	P2(1)/c	C2/c	
Unit cell dimensions			
a (Å)	14.434(1)	17.6692(13)	
b (Å)	15.527(1)	14.6492(12)	
c (Å)	18.784(1)	18.1301(14)	
α (°)	90	90	
β (°)	111.151(3)	103.929(4)	
γ (°)	90	90	
Volume (Å ³)	3926(1)	4554.8(6)	
Z	4	4	
Calculated density	1.423 Mg/m ³	1.512 Mg/m ³	
Absorption coefficient	0.684 mm^{-1}	0.885 mm^{-1}	
F(000)	1744	2116	
Crystal size	$0.47 \times 0.27 \times 0.27 \text{ mm}^3$	$0.43 \times 0.33 \times 0.18 \text{ mm}^3$	
Theta range for data collection	2.02–26.44°	2.31 to 28.26°	
Limiting indices	$\begin{array}{l} -18 \leq h {\leq} 18, -19 \leq k {\leq} 19, \\ -23 \leq l {\leq} 23 \end{array}$	$\begin{array}{l} -21 \leq h \leq 23, -19 \leq k \leq 19, \\ -24 \leq l \leq 24 \end{array}$	
Reflections collected/unique	69469/8050 [R(int) = 0.0656]	46244/5559 [R(int) = 0.0602]	
Completeness to theta $= 25.00$	99.9 %	98.4 %	
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	
Max. and min. transmission	1.000000 and 0.884555	1.000000 and 0.876297	
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2	
Data/restraints/parameters	8050/0/544	5559/117/365	
Goodness-of-fit on F^2	1.088	1.164	
Final R indices [I > 2sigma(I)]	R1 = 0.0426, wR2 = 0.1096	R1 = 0.0586, wR2 = 0.1476	
R indices (all data)	R1 = 0.0561, wR2 = 0.1236 $R1 = 0.0791, wR2 = 0.159$		
Largest diff. peak and hole	$0.513 \text{ and } -0.524 \text{ e.A}^{-3}$	1.159 and $-0.923 \text{ e.}\text{\AA}^{-3}$	

were carried out using a Perkin-Elmer Model 2400 CHNS/O elemental analyzer. Conductance measurements were performed using a Hanna HI 8820 conductivity meter. ¹H and ¹³C NMR spectra were obtained in CDCl₃ on a Bruker Avance 300 MHz and Jeol 90 MHz spectrometer using Si(CH₃)₄ as an internal standard.

X-ray crystallography

Vapor diffusion of diethyl ether into solutions of [CuL] and [ZnL] in chloroform and acetonitrile, respectively, afforded green and yellow prismatic crystals suitable for study by X-ray crystallography. Single-crystal X-ray diffraction analyses were performed on a Bruker Kappa APEX-II system at 89(2) K using graphite monochromated Mo-Ka X-ray radiation with exposures over 0.5°. Data were corrected for Lorentz and polarization effects using SAINT [30] and for absorption using SADABS [31]. All structures were solved using SIR-97 [32] within the WinGX [33] package, and weighted full-matrix refinement on F^2 was carried out using SHELXL-97 [34]. Hydrogen atoms were included in calculated positions and refined as riding with individual (or group, if appropriate) isotropic displacement parameters. Disorder was apparent in the naphthalene rings of [CuL]·2CHCl₃, with the rings displaying slight conformational mobility about C15; this was successfully modeled as a 50:50 distribution of the two conformations. Details of the X-ray experiments and crystal data are summarized in Table 1.

Synthesis of H₂L

A solution of 2,2'-(1,1'-binaphthyl-2,2'-diylbis(oxy))dianiline (0.468 g, 1 mmol) in methanol (20 ml) was added dropwise with stirring to a solution of o-vanillin (0.304 g, 2 mmol) in methanol (30 ml). The mixture was stirred and heated to reflux for 12 h. The resulting yellow precipitate was filtered off, washed with cold methanol, and dried in vacuo. Yield: 0.5 g (68 %). M.p. 108 °C. Anal. Calc. for $C_{48}H_{36}N_2O_6$: C, 78.2; H, 4.9; N, 3.8. Found: C, 78.9; H, 4.7; N, 4.1 %. IR (cm⁻¹, KBr): 1614 (s, vC=N). ¹H NMR (90 MHz, CDCl₃): δ 3.8 (s, 6H, H₂₃), 6.4–8.0 (m, 26H, aromatics), 8.1 (s, 2H, CH=N), 13.2 (s, 2H, OH). UV–Vis [λ (nm), ϵ (M⁻¹ cm⁻¹)]: 275 (48723).

Synthesis of [CuL]·2CHCl₃

A methanol solution (30 ml) of Cu(NO₃)₂·6H₂O (0.296 g, 1 mmol) was added to a warm solution of [H₂L] (0.737 g, 1 mmol) in methanol (50 ml). The mixture was stirred and heated to reflux for 12 h. The resultant green solid was collected by filtration, washed with cold methanol, and dried in vacuum. Yield: 0.7 g (68 %). M.p. 299 °C. Anal. Calc. for C₅₀H₃₆Cl₆CuN₂O₆ (MW: 1037.09): C, 57.9; H, 3.5; N, 2.7. Found: C, 57.5; H, 3.7; N, 3.1 %. IR (cm⁻¹, KBr): 1606 (s, vC=N). UV–Vis [λ (nm), ϵ (M⁻¹ cm⁻¹)]: 294 (39445), 398 (14850), 658 (62). $\Lambda_m = 1.3$ cm² Ω^{-1} mol⁻¹.

Synthesis of [ZnL]·CH₃CN

The preparation of the yellow microcrystalline complex followed the same procedure described for [CuL]·2CHCl₃ by using a solution of Zn(NO₃)₂·6H₂O (0.297 g, 1 mmol) in 30 mL of methanol. Yield: 0.6 g (71.3 %). M.p. 315 °C. Anal. Calc. for C₅₀H₃₇ZnN₃O₆ (MW:841.26): C, 71.4; H, 4.4; N, 5.0. Found: C, 71.5; H, 4.3; N, 4.8 %. IR (cm⁻¹, KBr): 1608 (s, vC=N). ¹H NMR (300 MHz, d6-DMSO): δ 3.7 (s, 6H, H₂₃), 6.5–7.8 (m, 26H, aromatics), 8.0 (s, 2H, CH=N). UV–Vis [λ (nm), ϵ (M⁻¹ cm⁻¹)]: 300(30213), 403(13221). $\Lambda_{\rm m} = 2.5$ cm² Ω^{-1} mol⁻¹.

Results and discussion

A new Schiff base H_2L (Fig. 1) has been prepared from the reaction of 2,2'-(1,1'-binaphthyl-2,2'-diylbis(oxy))dianiline and o-vanillin, in refluxing methanol. Elemental analysis and NMR spectrometry (see below) confirmed its formula and purity. Complexes of this ligand with Cu(II) and Zn(II) were synthesized by direct reactions of Cu(NO₃)₂·6H₂O and Zn(NO₃)₂·6H₂O with the ligand in an equimolar ratio in methanol solvent or template reactions starting from the respective metal salts, o-vanillin, and 2,2'-(1,1'-binaphthyl-2,2'-diylbis(oxy))dianiline in 1:1:1 mol ratio. Characterization of the complexes was achieved by IR spectroscopy, elemental analysis, molar conductance, UV-Vis spectra, NMR spectrometry (Zn complex), and X-ray crystal diffraction, all of which gave results consistent with the proposed formulations. The compositions of the products were not affected by changing the mole ratio of the reactants. The



Fig. 1 Structure of H₂L ligand, along with NMR numbering

complexes are soluble in CHCl₃, EtOH, MeOH, and THF and are non-electrolytes, as determined by molar conductivity measurements.

Spectroscopic and conductivity data

The IR spectra of both complexes show a sharp band in the range 1,606–1,608 cm⁻¹, attributed to v(C=N), which is shifted to lower frequency compared to the free ligand $(1,614 \text{ cm}^{-1})$. This is indicative of coordination of the imine nitrogen with the metal. Furthermore, the absence of C=O and N–H stretching vibrations in the spectra of the complexes confirms the Schiff base condensation. Deprotonation of the phenolic functions is confirmed by the lack of O–H stretching bands in the region 3,400–3,300 cm⁻¹ for both complexes [35, 36]. A band at 1,179 cm⁻¹ for [H₂L] is ascribed to the phenolic C–O stretching vibrations; this band is shifted to lower frequencies (1,168–1,170) in the complexes due to O-metal coordination.

¹H and ¹³C NMR data for the free Schiff base, H₂L, and the diamagnetic complex [ZnL] in CDCl₃ are given in Table S1, while the NMR numbering of the atoms is shown in Fig. 1. Both ¹H and ¹³C NMR spectra of the H₂L and [ZnL] show only a single imine resonance (¹H: 8.1 ppm (H₂L), 8.0 ppm (ZnL); ¹³C:166.1 ppm (H₂L), 168.7 ppm (ZnL)), demonstrating the equivalence of the two imine environments. The ¹H NMR spectrum of the complex [ZnL] is very similar to that of the free ligand, with only slight shifts to lower fields seen for the ligand protons in coordination with zinc(II). Most notably, the signal for the imine proton in the zinc complex is shifted downfield with respect to the corresponding signal in

Compound	$_{max}(nm) (\epsilon)^a \lambda$			
	Intraligand (LL)	СТ	d–d	
[H ₂ L]	275 (48723)			
[CuL]	294 (39445)	398 (14850)	658 (62)	
[ZnL]	300 (30213)	403 (13221)		

Table 2 Electronic spectroscopy data (nm) for ligand H_2L and related complexes

 $^{\rm a}~{\rm Mol}^{-1}~{\rm cm}^{-1}$

the free ligand, indicating that the metal-nitrogen bond is retained in solution.

A total of 22 peaks are observed in the aromatic region of the ¹³C NMR spectrum (112.8–152.9 ppm) of the [ZnL] complex, consistent with the presence of twofold symmetry in this complex. In the ¹³C NMR spectrum of the free Schiff base, the region corresponding to aromatic rings carbons (115.4–153.4 ppm) has 11 peaks instead of 22. The ¹H spectrum of [ZnL] shows the loss of the phenolic OH signal observed at 13.2 ppm for free H₂L, indicating deprotonation of the phenolic OH in coordination with Zn²⁺.

The electronic spectra of the ligand and its metal complexes were recorded in CHCl₃. The bands below 300 nm are attributable to intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. In the electronic spectra of the complexes, the intraligand transitions are slightly shifted as a result of coordination. The electronic spectrum of the Cu(II) complex shows an absorption at 658 nm attributed to the ²Eg \rightarrow ²T₂g transition, characteristic of square planar geometry [37, 38]. The Zn(II) complex is diamagnetic without any d–d transitions. The spectra of both complexes show an intense band around 400 nm, due to a charge transfer transition [39–42]. The electronic spectral details of the complexes are given in Table 2.

The molar conductivity (Λ_M) values of the complexes were 1.3–2.5 Ω^{-1} mol⁻¹ cm², measured at 25 °C using 10^{-3} M solutions in CHCl₃ solvent. These low values indicate that both complexes are non-electrolytes [43, 44]. Hence, the Schiff base ligand is most probably coordinated with the copper(II) and zinc(II) centers as a doubly charged anion. This is consistent with deprotonation and coordination of the two phenolic OH groups [45].

X-ray crystal structures

Suitable crystals of [ZnL]·CH₃CN and [CuL]·2CHCl₃ were obtained from acetonitrile and chloroform solutions of the respective complexes by slow diffusion of diethyl ether. ORTEP views of the complexes are shown in Figs. 2 and 3, respectively. Crystallographic data and structure refinement parameters are given in Table 1, and selected bond distances and angles are given in Table 3.



Fig. 2 Molecular structure of [ZnL] showing 30 % probability thermal ellipsoids using ORTEP



Fig. 3 Molecular structure of [CuL] showing 30 % probability thermal ellipsoids using ORTEP

The structure of [CuL]·2CHCl₃ comprises a Cu(II) center coordinated with the two imine N atoms and the two phenolate O atoms of the Schiff base ligand. The N₂O₂ donor atoms lie in what is best described as a distorted square planar arrangement (despite the τ_4 value of 0.42, supposedly indicative of a seesaw geometry [46]) with the two N and two O donors both adopting a mutually pseudo-trans arrangement (O–Cu–O and N–Cu–N bond angles of 143.22(12)° and 158.23(14)°, respectively). The other angles about the metal are in the range 92.42(9)– 94.41(10)°. The Cu(1)–O(1) distance (1.9070(19) Å) is consistent with deprotonation and formal coordination as

Table 3 Selected bond lengths (Å) and bond angles (°) for complexes [CuL]·2CHCl₃ and [ZnL]·CH₃CN

Complex [ZnL]		Complex [CuL]	
Bond	Distance	Bond	Distance
N(1)–Zn(1)	2.0642(19)	Cu(1)–O(1)#1	1.9070(19)
N(2)–Zn(1)	2.037(2)	Cu(1)–O(1)	1.9070(19)
O(2)–Zn(1)	1.9556(17)	Cu(1)–N(1)	1.976(3)
O(3)–Zn(1)	2.4062(17)	Cu(1)–N(1)#1	1.976(3)
O(4)–Zn(1)	2.4181(17)		
O(5)–Zn(1)	1.9620(18)		
Bond	Angle	Bond	Angle
O(2)–Zn(1)–O(5)	105.76(7)	O(1)#1-Cu(1)-O(1)	143.22(12)
O(2)-Zn(1)-N(2)	102.60(7)	O(1)#1-Cu(1)-N(1)	92.42(9)
O(5)-Zn(1)-N(2)	94.46(7)	O(1)-Cu(1)-N(1)	94.41(10)
O(2)-Zn(1)-N(1)	93.38(8)	O(1)#1-Cu(1)-N(1)#1	94.41(10)
O(5)-Zn(1)-N(1)	96.69(8)	O(1)-Cu(1)-N(1)#1	92.43(9)
N(2)-Zn(1)-N(1)	157.24(8)	N(1)-Cu(1)-N(1)#1	158.23(14)
O(2)–Zn(1)–O(3)	157.01(7)		
O(5)-Zn(1)-O(3)	94.52(7)		
N(2)-Zn(1)-O(3)	86.17(7)		
N(1)-Zn(1)-O(3)	73.24(7)		
O(2)-Zn(1)-O(4)	86.52(7)		
O(5)-Zn(1)-O(4)	164.89(6)		
N(2)-Zn(1)-O(4)	73.91(7)		
N(1)-Zn(1)-O(4)	91.23(7)		
O(3)–Zn(1)–O(4)	75.43(6)		

phenoxide.¹ The distance between the Cu(II) center and the symmetry-related ether O(3) atoms (2.667 Å; the metal lies on a twofold axis) is at the very high end (top 3.3 %) of the range for Cu(II)–ether O bonds, and any Cu–O bonding is at best very weak² [48]. Other bond distances within the molecules are within the normal values for Schiff base complexes of copper(II) [47–52] or other metals [53–59].

In contrast to $[CuL] \cdot 2CHCl_3$, the Zn(II) center in $[ZnL] \cdot CH_3CN$ displays a distorted octahedral geometry, being bonded to two ether O atoms (O(3) and O(4)), two imino N atoms (N(1) and N(2)), and two phenolate O atoms (O(2) and O(5)). As found in $[CuL] \cdot 2CHCl_3$, both the imine N atoms are disposed trans to each other (bond angle 157.24(8)°) but the O(5)–Zn(1)–O(2) bond angle is much less than the corresponding angle in $[CuL] \cdot 2CHCl_3$ (105.76(7)°), and as a result, both the phenolate O atoms and the ether O atoms are

positioned mutually cis to each other. Coordination of the ether O atoms with the zinc is confirmed by bond distances of 2.4062(17) Å and 2.4181(17) Å.³ The Zn–N (imine) (2.037(2)–2.0642(19) Å) and Zn–N (phenolate) (1.9556(17)–1.9620(18) Å) bond lengths are comparable to corresponding distances reported in the literature (see footnote 1).

Conclusion

In the present work, we have synthesized and characterized a new potentially octadentate N_2O_6 Schiff base ligand and its complexes with zinc(II) and copper(II). Physico-chemical measurements confirm the 1:1 metal to ligand stoichiometry of the complexes. The molecular structures of both complexes have been revealed by single-crystal X-ray analysis. Both of these complexes are neutral and found to have quite different geometries. Thus, the zinc complex is in a distorted octahedral geometry, while the copper complex has distorted square planar geometry.

Acknowledgments We are grateful to the Faculty of chemistry of Bu-Ali Sina University, National Foundation of elites (BMN) and Ministry of science, Research & Technology of Iran, for financial support.

References

- 1. Chohan ZH, Sheazi SKA (1999) Synth React Inorg Met Org Chem 29:105–118
- Jayabalakrishnan C, Natarajan K (2001) Synth React Inorg Met Org Chem 31:983–995
- Jeeworth T, Wah HLK, Bhowon MG, Ghoorhoo D, Babooram K (2000) Synth React Inorg Met Org Chem 30:1023–1038
- Dharmaraj N, Viswanalhamurthi P, Natarajan K (2001) Transition Met Chem 26:105–109
- Colins CH, Lyne PM (1970) Microhiul methods. University Park Press, Baltimore, p 422
- Chang S, Galvin JM, Jacobsen EN (1994) J Am Chem Soc 116:6937–6938
- 7. Deng L, Jacobsen EN (1992) J Org Chem 57:4320-4323
- 8. Yoon H, Burrows CJ (1988) J Am Chem Soc 110:4087–4089
- 9. DiMauro EF, Kozlowski MC (2002) J Am Chem Soc 124:12668–12669
- Darensbourg DJ, Mackiewicz RM, Rodgers JL, Phelps AL (2004) Inorg Chem 43:1831–1833
- Darensbourg DJ, Mackiewicz RM, Phelps AL, Billodeaux DR (2004) Acc Chem Res 37:836–844
- 12. Chapman JJ, Day CS, Welker ME (2001) Eur J Org Chem 12:2273–2282
- 13. Temel H (2002) Trans Met Chem 27:609-612
- 14. Boghaei DM, Mohebi S (2002) Tetrahedron 58:5357-5366
- 15. Katsuki T (2003) Synlett 3:281-297

 $^{^1}$ Cu–O bonds to neutral phenol are, on average, significantly longer than those to deprotonated phenol. The respective average values in the CSD (Version 5.32, November (2010)) are 2.399 and 1.910 Å.

 $^{^2}$ There are 671 instances of Cu(II)–ether O bonds, with distances ranging from 1.932 to 2.885 Å (mean = 2.338 Å, UQ = 2.535 Å). CSD Version 5.33, November (2011).

 $^{^3}$ There are 743 instances of Zn(II)–ether O bonds, with distances ranging from 1.966 to 2.839 Å (mean = 2.232 Å, UQ = 2.426 Å). CSD Version 5.33, November (2011).

- 16. Cozzi PG (2004) Chem Soc Rev 33:410-421
- 17. Dubsky JV, Sokol A (1931) Collect Czech Chem Commun 3:548
- 18. Barbieri GA, Ferrari C (1936) Ricerca sci 7:390
- 19. Tsuchida R, Tsumaki T (1938) Bull Chem Soc Jpn 13:527-533
- 20. Bailes RH, Calvin M (1947) J Am Chem Soc 69:1886-1893
- Zhang W, Loebach JL, Wilson SR, Jacobsen EN (1990) J Am Chem Soc 112:2801–2803
- Jacobsen EN, Zhang W, Muci AR, Ecker JR, Deng L (1991) J Am Chem Soc 113:7063–7064
- Schaus SE, Brandes BD, Larrow JF, Tokunaga M, Hansen KB, Gould AE, Furrow ME, Jacobsen EN (2002) J Am Chem Soc 124:1307–1315
- 24. Jacobsen EN (2000) Acc Chem Res 33:421-431
- Keypour H, Shayesteh M, Sharifi-Rad A, Salehzadeh S, Khavasi H, Valencia L (2008) J Organomet Chem 693:3179–3187
- 26. Yang C-P, Wei C-H (2001) Polymer 42:1837-1848
- 27. Liaw D-J, Liaw B-Y (1998) Polymer 39:1597-1607
- 28. Eastmond GC, Paprotny J (2004) Polymer 45:1073-1078
- 29. Tsuzuki H, Tsukinoki T (2001) Green Chem 3:37-38
- 30. SAINT, Bruker AXS Inc. (2005) Madison, Wisconsin
- 31. Sheldrick GM (1996) SADABS. University of Göttingen, Germany
- Altomare A, Burla MC, Camalli M, Cascarano GL, Giacovazzo C, Guagliardi A, Moliterni AGG, Polidori G, Spagna R (1999) J Appl Crystallogr 32:115–119
- 33. Farrugia LJ (1999) J Appl Cryst 32:837-838
- 34. Sheldrick GM (2008) Acta Crystallogr Sect A 64:112-122
- 35. Nakamoto K (1977) Infrared and Raman spectra of inorganic and coordination compound, 3rd edn. Wiley Interscience, NY
- Ali SA, Soiman AA, Aboaly MM, Ramandan RM (2002) J Coord Chem 55:1161–1170
- 37. Ilhan S, Temel H, Kilic A, Tas E (2007) Transit Metal Chem 32:1012–1017

- 38. Temel H, Ilhan S, Kilic A, Tas E (2008) J Coord Chem 61:1443–1454
- Suni V, Prathapachandra Kurup MR, Nethaji M (2007) Polyhedron 26:5203–5209
- Lever ABP (1984) Inorganic electronic spectroscopy, 2nd edn. Elsevier, New York
- 41. Maki AH (1958) J Chem Phys 28:651-662
- 42. Guidote AM Jr, Ando K-I, Terada K, Kurusu Y, Nagao H, Masuyama Y (2001) Inorg Chim Acta 324:203–211
- 43. Geary W (1971) J Chem Rev 7:81-122
- 44. Tas E, Aslanoglu M, Kilic A, Kaplan O, Temel H (2006) J Chem Res (S) 4:242–245
- 45. Ali MA, Mirza AH, Butcher RJ (2001) Polyhedron 20:1037-1043
- 46. Yang L, Powell DR, Houser RP (2007) Dalton Trans 9:955-964
- 47. Akitsu T, Einaga Y (2004) Acta Crystallogr Sect E 60:m436
- 48. Akitsu T, Einaga Y (2004) Acta Crystallogr Sect E 60:m1552
- 49. Akitsu T, Einaga Y (2004) Acta Crystallogr Sect E 60:m1555
- 50. Akitsu T, Einaga Y (2004) Acta Crystallogr Sect E 60:m1602
- 51. Akitsu T, Einaga Y (2004) Acta Crystallogr Sect C 60:m640
- 52. Akitsu T, Einaga Y (2006) Polyhedron 25:1089-1095
- 53. Yamada S (1999) Coord Chem Rev 537:190-192
- Sakiyama H, Okawa H, Matsumoto N, Kida S (1990) J Chem Soc Dalton Trans 2935-2939
- 55. Bosnich B (1968) J Am Chem Soc 90:627-632
- 56. Okawa H, Nakamura M, Kida S (1986) Inorg Chim Acta 120:185–189
- 57. Nishida Y, Kida S (1970) Bull Chem Soc Jpn 43:3814-3819
- Sakiyama H, Okawa H, Matsumoto N, Kida S (1991) Bull Chem Soc Jpn 64:2644–2647
- 59. Ulusoy M, Karabiyik H, Kilincarslan R, Aygun M, Cetinkaya B, Garcia-Granda S (2008) Struct Chem 19:749