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Note

# Complexes of Cu(II), Co(II) and Ni(II) with pyrazole-derived ligands. Crystal structure of {bis[3-phenyl-5-(2-pyridyl)pyrazolato, $\kappa N^1:\kappa N^2$ ]copper(II)}

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#### Abstract

The reaction of the pyrazole derived-ligands 3-phenyl-5-(2-pyridyl)pyrazole (HL<sup>0</sup>) and 3-phenyl-5-(6-methyl-2-pyridyl)pyrazole (HL<sup>1</sup>) with Cu(CH<sub>3</sub>COO)<sub>2</sub>, Co(CH<sub>3</sub>COO)<sub>2</sub> and Ni(CH<sub>3</sub>COO)<sub>2</sub> was carried out. Products were characterised by elemental analyses, conductivity measurements and infrared and electronic spectroscopy. The IR spectra of complexes display the typical absorption bands of pyrazole-derived ligands. The nature of the complexes depends on the metal, M, the ligand, HL, and the M:HL ratio: Ni(HL)<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>, Cu(L)<sub>2</sub>, (HL = HL<sup>0</sup>, HL<sup>1</sup>), Co(L<sup>0</sup>)<sub>2</sub>. In the complexes of Co(II) and Cu(II) the pyrazole is deprotonated, the band v(N-H) was not observed in IR spectroscopy. The crystal structure of [Cu(L<sup>0</sup>)<sub>2</sub>] consists of discrete centrosymmetric molecules involving a co-ordinated CuN(pz)<sub>2</sub>N(py)<sub>2</sub> core with planar geometry. The anionic ligand L<sup>0</sup> is not completely planar. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Copper, cobalt and nickel complexes; Pyrazole complexes; Crystal structures

# 1. Introduction

The chemistry of pyrazole and pyrazolate metal complexes is quite extensive in the literature [1-5].

The pyrazolate ligand can exhibit three co-ordination modes. It can act as a monodentate (pyrazole-N) and *exo*-bidentate (pyrazole N,N') or an *endo*-bidentate ligand [1,2]. In most cases, the pyrazolate ligand co-ordinates in an *exo*-bidentate fashion, thus linking two metal centres that may be identical or different.

Recent studies have described the catalytic activity of pyrazolate complexes [2,3] under mild conditions, thus encouraging the exploration of the pyrazolate ligand.

The 3,5-substituted pyrazolic ligands have been extensively investigated in our laboratory during the last decade [6–13], in particular the synthesis and characterisation of the ligands 3-phenyl-5-(2-pyridyl)pyrazole (HL<sup>0</sup>), 3-phenyl-5-(6-methyl-2-pyridyl) pyrazole (HL<sup>1</sup>), 3,5-bis(2-pyridyl)pyrazole (HL<sup>2</sup>), 3-(6-methyl-2-pyridyl)-5-(2-pyridyl)pyrazole (HL<sup>3</sup>) and 3,5-bis-2-(6-methylpyridyl)pyrazole (HL<sup>4</sup>). These molecules have been studied as co-ordination ligands to divalent transition metals: Co(II), Ni(II), Cu(II), Zn(II), Pd(II) and Cd(II). Munakata et al. have also described three complexes with the HL<sup>3</sup> ligand; two of Ag(I) and one of Cu(II) [14].

In spite of the significant results on the co-ordination ability of pyridyl-pyrazole HL ligands, it is difficult to predict the product of their reaction with transition metal salts. This difficulty increases when the anion is

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Fig. 1. Pyrazole derived ligands HL<sup>0</sup> and HL<sup>1</sup>.

also a co-ordinating ligand like the acetate group. Previous studies of the reactivity of HL ligands with metal acetate salts report different results: whereas in the case of Pd(II) a Pd<sub>2</sub>L<sub>4</sub><sup>1</sup> compound is obtained [11], the reaction of Cu(CH<sub>3</sub>COO)<sub>2</sub> with the ligand 3-(2-pyridyl)pyrazole produces a tetranuclear Cu(II) complexes  $[Cu_4(L)_6(solv)_2][PF_6]_2$  (solv = DMF or MeOH) [15,16]. In order to explore the bonding possibilities of both HL and acetate ligands we studied the reactivity of some transition metal acetates with pyridyl-pyrazole ligands. Here we present the results of the reactions of Ni(II), Cu(II) and Co(II) acetates with the HL<sup>0</sup> and HL<sup>1</sup> ligands.

## 2. Experimental

### 2.1. General methods

All reactions were performed out with the use of vacuum line and Schlenk techniques. Elemental analysis was carried out by the staff of the Chemical Analysis Service of the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 apparatus. IR spectra were obtained on a Perkin–Elmer 2000 spectrometer with

Table 1							
Physical	and	analytical	data	for	the	com	olexes

KBr pellets in the region  $4000-100 \text{ cm}^{-1}$ . The conductivity measures were taken with a Radiometer CDM-3 conductimeter. The electronic spectra in solution were run on a Kontron–Uvikon 860 in different solvents between 750 and 350 nm. The electronic spectra in solid state (KBr pellets, diffuse reflectance) were obtained on a Kontron–Tegimenta CH-6343 Rotkreuz AG.

## 2.2. Synthesis of ligands

The compounds 3-phenyl-5-(2-pyridyl)pyrazole (HL<sup>0</sup>) and 3-phenyl-5-(6-methyl-2-pyridyl)pyrazole (HL<sup>1</sup>) were synthesised as reported previously [10] (Fig. 1).

# 2.3. Synthesis of the metal complexes

# 2.3.1. Complexes $Ni(HL)_2(CH_3COO)_2 \cdot xH_2O$ where $HL = HL^0$ , x = 2 (1) and $HL = HL^1$ , x = 0 (2)

The appropriate ligand (0.45 mmol:  $HL^0$ , 0.10 g;  $HL^1$ , 0.11 g) dissolved in ethanol (20 ml) was added to a solution of Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (0.22 mmol, 0.054 g) in ethanol (10 ml). The resulting solution was stirred at room temperature (r.t.) for 10 h and concentrated on a vacuum line to one-fifth of the initial volume; crystalline solids were obtained which were filtered off and dried in vacuum, washed with THF and dried in vacuo. The same products (formula and yield, Table 1) were obtained when a 1:1 Ni:HL ratio was used.

1: IR(KBr): v(N-H) 3205;  $v(C-H)_{ar}$  3064; v(C=C), v(C=N) 1608, 1571;  $v_{as}(COO)$  1593;  $v_{s}(COO)$  1384;  $\delta(COO)$  988;  $\delta(C-H)_{oop}$  762;  $v_{as}(Ni-O)$  491,  $v_{as}(Ni-N)$ 422;  $v_{s}(Ni-O)$  310, 260;  $v_{s}(Ni-N)$  230 cm<sup>-1</sup>. UV–Vis (methanol 3.92 × 10<sup>-3</sup> M),  $\lambda(\varepsilon)$ : 618(15), 587(21), 346(sh) nm; (DMF 2.03 × 10<sup>-3</sup> M),  $\lambda(\varepsilon)$ : 602(21),

Compound	Colour	Yield (%)	Analysis <sup>a</sup>			Conductivity <sup>b</sup> ( $\Omega^{-1}$ cm <sup>2</sup> mol <sup>-1</sup> )	
			C (%)	N (%)	Н (%)	_	
$Ni(HL^0)_2(CH_3COO)_2 \cdot 2H_2O$ (1)	green	35	(58.65)	(12.82)	(4.92)	48 °	
· /2· 5 /2 2 · /	e		58.18	12.16	4.39	5 d	
$Ni(HL^1)_2(CH_3COO)_2$ (2)	green	45	(63.09)	(12.99)	(4.95)	66 °	
, ,2, 5 ,2,,	e		63.40	12.78	4.90	5 d	
$Cu(L^0)_2$ (3)	brown	87	(66.72)	(16.67)	(3.99)	8 <sup>d</sup>	
( )2()			66.65	16.54	4.10	3 °	
$Cu(L^{1})_{2}$ (4)	brown	52	(67.73)	(15.80)	(4.51)	10 <sup>d</sup>	
			67.49	15.48	4.30	6 °	
$Co(L^0)_2 \cdot 2H_2O$ (5)	brown	50	(62.81)	(15.69)	(4.52)	6 <sup>d</sup>	
			62.69	15.07	3.86	6 <sup>f</sup>	

<sup>a</sup> Calculated analytical values are given in parentheses.

<sup>b</sup> The reported values for 1:1 electrolyte in methanol is 80–115  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, in DMF is 65–90  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, in DMSO is 50–70  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> and, in acetonitrile the values are 120–160  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, respectively [19,20].

 $^{\rm c} 10^{-3}$  M in methanol.

<sup>d</sup>  $10^{-3}$  M in DMF.

 $e 10^{-3}$  M in DMSO.

 $^{\rm f} 10^{-3}$  M in acetonitrile.

Table 2

Crystallographic data and structure refinement	or	3
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Compound	$Cu(L^0)_2$			
Empirical formula	$C_{28}H_{20}CuN_6$			
Formula weight	504.04			
Temperature (K)	293(2)			
Wavelength	0.71069			
Crystal system	monoclinic			
Space group	$P2_{1}/c$			
Unit cell dimensions				
a (Å)	13.0448(13)			
b (Å)	5.2963(6)			
<i>c</i> (Å)	16.384(3)			
β_(°)	103.364(11)			
$V(Å^3)$	1101.3(3)			
Ζ	2			
$D_{\rm calc} \ ({\rm Mg} \ {\rm m}^{-3})$	1.520			
Absorption coefficient (mm <sup>-1</sup> )	0.102			
Crystal size (mm)	$0.47 \times 0.47 \times 0.30$			
Unique reflections	1940			
Goodness-of-fit on $F^2$	1.121			
Final R indices $[I > 2\sigma(I)]$	R(F) = 0.026,			
	$R_{\rm w}(F^2) = 0.079$			
R indices (all data)	R(F) = 0.030,			
	$R_{\rm w}(F^2) = 0.080$			
Largest difference peak and hole (e $Å^{-3}$ )	0.19, -0.16			

569(17), 364(sh) nm. UV–Vis (KBr):  $\lambda = 706$ , 616, 570, 370 nm.

**2**: IR(KBr): v(N-H) 3119;  $v(C-H)_{ar}$  3049; v(C=C), v(C=N) 1608, 1577;  $v_{as}(COO)$  1615,  $v_{s}(COO)$  1396;  $\delta(COO)$  888;  $\delta(C-H)_{oop}$  775;  $v_{as}(Ni-O)$  533,  $v_{as}(Ni-N)$ 434, 378;  $v_{s}(Ni-O)$  286;  $v_{s}(Ni-N)$  244 cm<sup>-1</sup>. UV–Vis (methanol 5.22 × 10<sup>-3</sup> M),  $\lambda(\varepsilon)$ : 631(15), 592(19), 351(sh) nm; (DMF 2.03 × 10<sup>-3</sup> M),  $\lambda(\varepsilon)$ : 688(14), 658(15), 365(sh) nm. UV–Vis (KBr):  $\lambda = 716$ , 618, 592, 370 nm.

2.3.2. Complexes  $ML_2 \cdot xH_2O$  where M = Cu,  $L = L^0$ and x = 0 (3), M = Cu,  $L = L^1$  and x = 0 (4), M = Co,  $L = L^0$  and x = 2 (5)

An amount of ligand (0.45 mmol:  $HL^0$ , 0.10 g;  $HL^1$ , 0.11 g) dissolved in 10 ml of ethanol, was added to a solution of the corresponding metallic salt (0.22 mmol, 0.054 g of Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O or 0.044 g of Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O) in 10 ml of ethanol. The mixture was stirred for 20 h and the precipitate was filtered off, washed with ethanol and ether and dried in vacuo.

3: IR(KBr):v(O-H) 3400;  $v(C-H)_{ar}$  3088; v(C=C), v(C=N) 1612, 1547;  $\delta(C-H)_{oop}$  758;  $v_{as}(Cu-N)$  420;  $v_{s}(Cu-N)$  250 cm<sup>-1</sup>. UV–Vis (DMF 1.98x10<sup>-3</sup> M),  $\lambda(\epsilon)$ : 585(49), 366(sh) nm.

4: IR(KBr): $\nu$ (O–H) 3392;  $\nu$ (C–H)<sub>ar</sub> 3090;  $\nu$ (C=C),  $\nu$ (C=N) 1610, 1553;  $\delta$ (C–H)<sub>oop</sub> 765;  $\nu$ <sub>as</sub>(Cu–N) 432;  $\nu$ <sub>s</sub>(Cu–N) 252 cm<sup>-1</sup>. UV–Vis (DMF 1.98x10<sup>-3</sup> M),  $\lambda$ (ε): 612(65), 356(sh) nm. 5: IR(KBr):v(O-H) 3392;  $v(C-H)_{ar}$  3095; v(C=C), v(C=N) 1613, 1548;  $\delta(C-H)_{oop}$  760;  $v_{as}(Co-N)$  314;  $v_{s}(Co-N)$  228 cm<sup>-1</sup>. UV–Vis (KBr):  $\lambda = 670$ , 400 nm.

# 2.4. X-ray crystal structure analyses

Suitable crystals for X-ray diffraction experiments of compound Cu(L<sup>0</sup>)<sub>2</sub> **5** were obtained by crystallisation from ethanol. One crystal was mounted on an Enraf– Nonius CAD4 diffractometer. Intensities were collected using the  $\omega$ -2 $\theta$  scan mode to  $2\theta_{max} = 50^{\circ}$ . Graphitemonochromated Mo K $\alpha$  radiation was used. The structure was solved by direct methods (SHELXS-86) [17] and refined by full-matrix least-squares methods on  $F^2$  for all reflections (SHELXL-97) [18]. The final R(F) and  $R_w(F^2)$  values as well as the number of parameters refined and other details concerning the refinement of the crystal structure are presented in Table 2. The weight was  $w^{-1} = \sigma^2(F_o^2) + (0.0483P)^2 + 0.1764P$ where  $P = (F_o^2 + 2F_c^2)/3$ .

#### 3. Results and discussion

# 3.1. Synthesis and spectroscopic properties of the complexes

The reaction of  $HL^0$  and  $HL^1$  ligands with  $M(CH_3COO)_2$  (M = Co, Ni and Cu) salts gives different types of complex depending on the metal, the ligand and the metal to ligand (M:HL) ratio.

Ni(CH<sub>3</sub>COO)<sub>2</sub> reacts with HL<sup>0</sup> and HL<sup>1</sup> ligands in different M:HL ratios to produce a sole type of complex: Ni(HL)<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub> (HL = HL<sup>0</sup> (1) and HL<sup>1</sup> (2)). Cu(CH<sub>3</sub>COO)<sub>2</sub> and HL ligands react to form the Cu(L)<sub>2</sub> (3, 4) complexes. The reactivity of Co(CH<sub>3</sub>COO)<sub>2</sub> with HL<sup>0</sup> in a 1:2 ratio leads to a Co(L<sup>0</sup>)<sub>2</sub>·2H<sub>2</sub>O (5) complex. Reactions at other ratios do not give pure products. This study shows that Ni(II) complexes contain the pyrazole derived ligand in its neutral form whereas Cu(II) and Co(II) form compounds with anionic L<sup>0</sup> and L<sup>1</sup> ligands. Table 1 gives analytical and conductivity data for the complexes synthesised.

Conductivity data for complexes 1-5 in several solvents show non-ionic behaviour consistent with neutral products.

The IR spectra of the complexes show the absorption bands assigned to the asymmetric and symmetric v(OCO) stretching modes and the typical bands of HL pyrazole-derived ligands [10]. Complexes **1**, **2** display two well defined bands between 1615–1590 and 1396– 1381 cm<sup>-1</sup>, separated by  $\Delta = v_{as}(OCO) - v_s(OCO) =$ 219–200 cm<sup>-1</sup>. These  $\Delta$  values suggest the presence of unidentate acetate groups in compounds **1**, **2** [21–23]. The IR spectra of complexes **1** and **2** show the v(NH) absorption at 3205 and 3119 cm<sup>-1</sup>, respectively, which implies the neutral nature of HL ligands.

Electronic spectra of Ni(II) complexes (1 and 2) were measured in methanol and DMF solutions and with KBr pellets (diffuse reflectance). Both Ni(II) complexes show two absorptions in the visible region between 688 and 569 nm ( $\varepsilon = 14-21 \text{ mol}^{-1} \text{ cm}^{-1}$  l) which are characteristic for octahedral Ni(II) complexes [24–26]. Electronic spectra using diffuse reflectance methods show an additional band at 716–706 nm which can be assigned to the  ${}^{3}A_{2g} \rightarrow {}^{1}E_{g}(D)$  transition of the d<sup>8</sup> ion an octahedral field [27].

Complex **5** is insoluble in methanol so we registered its electronic spectrum using a diffuse reflectance method. This complex displays one band at 670 nm which is typical for octahedral Co(II) centres [24,25,28,29].

# 3.2. Crystal structure of $[Cu(L^0)_2]$

Fig. 2 shows the molecular structure of compound **3**  $(Cu(L^0)_2)$ . The crystal structure consists of discrete centrosymmetric  $Cu(L^0)_2$ . The literature contains seventeen structures of complexes with 5-(2-pyridyl)pyrazole ligand with a R = H, Me, 'Bu, Ph and py group bonded to the pyrazole ring at position 3. In these structures the pyrazole ligand can adopt three modes of co-ordination: anionic monodentante [15,16,30,31], neutral monodentate [10,12,13] and *exo*-bidentate [6,8,11,14,32–36].

The structure of **3** has two 3-phenyl-5-(2pyridyl)pyrazolato ligand in a trans disposition bonded to a Cu(II) centre in a bidentate co-ordination mode by the N10(py) and N20(pz) atoms. This co-ordination mode involves a CuN<sub>4</sub> core with distorted square planar geometry. Each anionic L<sup>0</sup> ligand is bonded to metal using two of its three co-ordinating nitrogen atoms (N(py) and N(pz)). The metal–ligand bond distances are 2.0450(15) Å (Cu–N10(py)) and 1.9440(15)



Å (Cu–N20(pz)), respectively. These values are consistent with those described in the literature (1.974-2.109 Å for Cu–N(py)) [8,14,15,37–39] and (1.929-2.088 Å for Cu–N(pz)) [8,14,15,29,40–42]. Nevertheless the Cu–N20(pz) bond length is shorter than the Cu–N(pz) distance (1.972(2) Å) found in this complex. It is also shorter than the Cu–N(pz) in the complex [Cu(HL<sup>0</sup>)(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>] (NO<sub>3</sub>) [13] where HL<sup>0</sup> is neutral.

The N10–Cu–N20 bite angle of  $80.95(6)^{\circ}$  is similar to those found in other complexes with HL<sup>0</sup> and HL<sup>1</sup> ligands [10–13]. The HL<sup>0</sup> ligands are not completely planar in this structure. The pyridyl and phenyl groups are slightly twisted around the pyrazole ring: Thus, the angles between aromatic rings found in the structure are: py–pz 5.70(10)°, py–ph 9.07(10)° and pz–ph 3.68(11)°. These angles are comparable to those found in the structure [Cu(HL<sup>0</sup>)(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>) [13].

The structure of 3 is very similar to that of the complex  $PdL_2$  where HL = 3-(2square-planar pyridyl)pyrazole [30]. In this case, the presence of two hydrogen bonds was considered to stabilise the planar configuration. In complex 3 the square-planar geometry of Cu(II) may also be favoured by hydrogen bonds between C15–H and N21<sup>i</sup> (the C15–H bond length has been geometrically fixed in the refinement (0.93 Å) and the contact parameters between C15-H and N21 are: H…N21<sup>i</sup>, 2.29 Å; C15…N21<sup>i</sup>, 3.079(3) Å; C15-H···N21<sup>i</sup>, 142°; symmetry code (i): -x, -y, -z). It is interesting to point out that the reaction of 3-(2pyridyl)pyrazole ligand with Cu(CH<sub>3</sub>COO)<sub>2</sub> led to the formation of  $[Cu_4(L)_6 (solv)_2][PF_6]_2 (solv = DMF or$ MeOH) complexes (the structure of which was established by X-ray diffractometry [15,16]) in contrast to its reaction with Pd(CH<sub>3</sub>COO)<sub>2</sub>, which gives a PdL<sub>2</sub> complex [30].

#### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 162862. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033; e-mail: deposit@ aadc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk].

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#### References

- [1] S. Trofimenko, Prog. Inorg. Chem. 34 (1986) 115.
- [2] S. Trofimenko, Chem. Rev. 93 (1993) 943.
- [3] G. La Monica, G.A. Ardizzoia, Prog. Inorg. Chem. 46 (1997) 151.
- [4] R. Mukherjee, Coord. Chem. Rev. 203 (2000) 151.
- [5] S. Trofimenko, Chem. Rev. 72 (1972) 497.
- [6] J. Casabó, J. Pons, K. Siddiqi, F. Teixidor, E. Molins, C. Miravitlles, J. Chem. Soc., Dalton Trans. (1989) 1401.
- [7] J. Pons, X. López, E. Benet, J. Casabó, F. Teixidor, F.J. Sánchez, Polyhedron 9 (1990) 2839.
- [8] J. Pons, X. López, J. Casabó, F. Teixidor, A. Caubet, J. Rius, C. Miravitlles, Inorg. Chim. Acta 195 (1992) 61.
- [9] J. Pons, F.J. Sánchez, A. Labarta, J. Casabó, F. Teixidor, A. Caubet, Inorg. Chim. Acta 208 (1993) 167.
- [10] A. Chadghan, J. Pons, A. Caubet, J. Casabó, J. Ros, A. Alvarez-Larena, J.F. Piniella, Polyhedron 19 (2000) 855.
- [11] J. Pons, A. Chadghan, J. Casabó, A. Alvarez-Larena, J.F. Piniella, J. Ros, Inorg. Chem. Commun. 3 (2000) 296.
- [12] J. Pons, A. Chadghan, J. Casabó, A. Alvarez-Larena, J.F. Piniella, X. Solans, M. Font-Bardia, J. Ros, Polyhedron 20 (2001) 1029.
- [13] J. Pons, A. Chadghan, A. Alvarez-Larena, J.F. Piniella, J. Ros, Polyhedron 20 (2001) 2531.
- [14] M. Munakata, L.P. Wu, M. Yamamoto, T. Kurodasowa, M. Maekawa, S. Kawata, S. Kitagawa, J. Chem. Soc., Dalton Trans. (1995) 4099.
- [15] K.L.V. Mann, E. Psillakis, J.C. Jeffery, L.H. Rees, N.M. Harden, J.A. McCleverty, M.D. Ward, D. Gatteschi, F. Totti, F.E. Mabbs, E.J.L. McInnes, P.C. Riedi, G.M. Smith, J. Chem. Soc., Dalton Trans. (1999) 339.
- [16] J.C. Jeffery, P.L. Jones, K.L.V. Mann, E. Psillakis, J.A. Cleverty, M.D. Ward, C.M. White, Chem. Commun. (1997) 175.
- [17] G.M. Sheldrick, SHELXS-86, Program for Crystal Structure Determination, University of Göttingen, Germany 1986.
- [18] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany 1997.
- [19] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.
- [20] L.K. Thompson, F.L. Lee, E.J. Gabe, Inorg. Chem. 27 (1988) 39.

- [21] G.B. Deacon, R.J. Phillips, Coord. Chem. Rev. 33 (1980) 227.[22] Q. Chen, J. Lynch, P. Gómez-Romero, A. Ben-Hussein, G.B.
- Jameson, C.J. O'Connor, L. Que, Inorg. Chem. 27 (1988) 2673.
- [23] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 4th ed., Wiley, New York, 1986.
- [24] D. Sutton, Electronic Spectra of Transition Metal Complexes, 1st ed., McGraw-Hill, UK, 1975.
- [25] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5th ed., Wiley, New York, 1988.
- [26] N.F. Curtis, Y.M. Curtis, Inorg. Chem. 4 (1965) 804.
- [27] W. Rosen, D.H. Busch, Inorg. Chem. 9 (1970) 262.
- [28] J.C. Bailar, H.J. Emeleus, S.R. Nythorm, A.F.T. Dickenson, Comprehensive Inorganic. Chemistry Board, 1st ed., Pergamon, Oxford, 1973.
- [29] J. Ferguson, Prog. Inorg. Chem. 12 (1970) 159.
- [30] M.D. Ward, J.S. Fleming, E. Psillakis, J.C. Jeffery, J.A. McCleverty, Acta Crystallogr., Sect. C 54 (1998) 609.
- [31] J. Sieler, H. Henning, Z. Anorg. Allg. Chem. 381 (1971) 219.
- [32] P.L. Jones, J.C. Jeffrey, J.A. McCleverty, M.D. Ward, Polyhedron 16 (1997) 1567.
- [33] K. Singh, J.R. Long, P.J. Stavropoulus, J. Am. Chem. Soc. 119 (1997) 2942.
- [34] M.H.W. Lam, S.T.V. Cheung, K.M. Fung, W.T. Wong, Inorg. Chem. 36 (1997) 4618.
- [35] E. Psillakis, J.C. Jeffrey, J.A. Cleverty, M.D. Ward, Chem. Commun. (1997) 1965.
- [36] A. Satake, H. Koshino, T. Nakata, J. Organomet. Chem. 595 (2000) 208.
- [37] P.J. van Konningsbruggen, D. Gatteschi, R.A.G. de Graaff, J.G. Haasnoot, J. Reedjick, C. Zanchini, Inorg. Chem. 34 (1995) 5175.
- [38] G. Munno, M. Julve, F. Lloret, J. Faus, M. Verdaguer, A. Caneschi, Angew. Chem., Int. Ed. Engl. 32 (1993) 1046.
- [39] K.J. Catalan, S. Jackson, J.D. Zubrowski, D.L. Perry, E.J. Valiente, L.A. Feliu, A. Polanco, Polyhedron 14 (1995) 2165.
- [40] H.H. Murray, R.G. Raptis, J.P. Fackler, Inorg. Chem. 27 (1988) 26.
- [41] S.M. Gorun, R.T. Stibrany, A.R. Katritzky, J.J. Slawinski, H. Faid-Allah, F. Brunner, Inorg. Chem. 35 (1996) 3.
- [42] P.M. Slangen, P.J. van Konningsbruggen, J.G. Haasnoot, J. Jansen, S. Gorter, J. Reedjick, H. Kooijman, W.J.J. Smeets, A.L. Spek, Inorg. Chim. Acta 212 (1993) 289.