

The Coordination Chemistry of Divalent Cobalt, Nickel and Copper.

Part 8. Selected Complexes Containing N-substituted Pyridine-2,6-dicarboxamide Ligands; Crystal Structure of Dibromo(*N,N'*-dimethyl-*N,N'*-diphenylpyridine-2,6-dicarboxamide)nickel(II)

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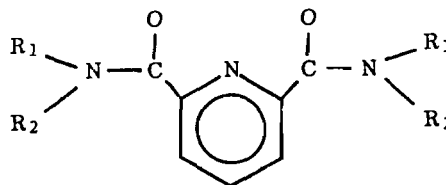
Abstract

Diverse complexes of divalent cobalt, nickel and copper and the ligands *N,N,N',N'*-tetramethylpyridine-2,6-dicarboxamide (tpda), *N,N'*-dimethyl-*N,N'*-diphenylpyridine-2,6-dicarboxamide (dpda) and *N,N,N',N'*-tetraisopropylpyridine-2,6-dicarboxamide (ppda) were discussed in order to illustrate the properties of these ligands. The complexes $[M(ppda)_2](ClO_4)_2$ ($M = Co, Ni$ and Cu) and $[Co(ppda)_2](ClO_4)_2(acet)$ ($acet = acetone$), had distorted octahedral chromophores. The distortion was most pronounced in $[Cu(ppda)_2](ClO_4)_2$. This severe distortion was not present in octahedral $[Ni(tpda)_2](ClO_4)_2$. Isostructural, crystalline $(MCl_2)_3(tpda)_2$ ($M = Ni$ and Co) were isolated from hot solutions. The solid reflectance spectra were resolved into gaussian components. This data, in conjunction with infrared and magnetic measurements, enabled the assignment of the formula $[MCl(tpda)]_2[MCl_4]$ to these complexes. The anion was found to be tetrahedral while the cation had a distorted tetrahedral chromophore. The reaction of $NiBr_2$ with dpda produced two complexes; green $\alpha NiBr_2(dpda)$ was isolated at room temperature while red $\beta NiBr_2(dpda)$ was obtained from hot solution. Characterisation data indicated $\alpha NiBr_2(dpda)$ to have a pentacoordinate chromophore. The characterisation data for $\beta NiBr_2(dpda)$ was ambiguous and a crystal structure determination was performed (monoclinic crystal, space group $P2_1/a$ with $a = 13.871$, $b = 16.019$, $c = 9.878$ Å, $\beta = 95.492^\circ$, final R factor = 0.0549 and $N_{obs} = 2221$). The Ni was in a distorted square pyramidal environment with the donor atoms of dpda and a bromine atom constituting the basal plane and the remaining bromine atom occupying the apical position. The coordination spheres of the crystalline complexes $NiBr_2(dpda)(dmp)$ ($dmp = 2,2$ -dimethoxypropane) and $NiBr_2(dpda)(acet)$ were analogous to those of $\alpha NiBr_2(dpda)$ and $\beta NiBr_2(dpda)$ respectively.

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Introduction

The factors which lead to the stabilisation of low symmetry five-coordinate complexes when using neutral donor ligands have been studied over an extensive period in these laboratories [1, 2]. As part of this long term project, the potentially tridentate ligand *N,N,N',N'*-tetramethylpyridine-2,6-dicarboxamide (tpda), *N,N'*-dimethyl-*N,N'*-diphenylpyridine-2,6-dicarboxamide (dpda) and *N,N,N',N'*-tetraisopropylpyridine-2,6-dicarboxamide (ppda) were prepared and a large number of divalent cobalt, nickel and copper complexes with varying anions, were isolated and studied.



tpda: $R_1 = R_2 = \text{methyl}$

dpda: $R_1 = \text{methyl}; R_2 = \text{phenyl}$

ppda: $R_1 = R_2 = \text{isopropyl}$

Some of the results obtained during this investigation have already been reported [3–5]. In this paper the preparation, characterisation and nature of a selection of the remaining complexes are discussed. These compounds exhibit some puzzling features and give perspective pertaining to the ligand properties. Although the donor atoms of all three ligands are similar, the degree of steric interaction at the carboxamide oxygen increases from tpda to dpda to ppda. These steric factors, in conjunction with lattice effects and the nature of the anions, are responsible for the variety in coordination spheres found in the complexes isolated.

Experimental

Preparation

The ligand, *N,N'*-dimethyl-*N,N'*-diphenylpyridine-2,6-dicarboxamide, was prepared by the dropwise addition of a solution of pyridine-2,6-dicarboxyl chloride (0.1 mol), dissolved in benzene (250 cm³), to *N*-methylaniline (0.6 mol) in benzene (350 cm³) under anhydrous conditions. The hydrochloride was removed by equilibrating the reaction mixture with aqueous sodium carbonate solution. After the benzene and excess *N*-methylaniline were removed by distillation, the impure dpda was recrystallised from acetone.

The ligands *N,N,N',N'*-tetramethylpyridine-2,6-dicarboxamide and *N,N,N',N'*-tetraisopropylpyridine-2,6-dicarboxamide were prepared in an analogous manner using dimethylamine (100 cm³ ampoule) and diisopropylamine, respectively.

In the following preparations, all solvents were dried over molecular sieves before use.

A solution of M(ClO₄)₂·6H₂O (1.0 mmol), where M = Co and Ni, dissolved in anhydrous ethanol (100 cm³) and 2,2-dimethoxypropane (20 cm³) was boiled down to a volume of 20 cm³. The ligand ppda (2.2 mmol) in hot acetone (50 cm³) was added. This solution was stirred and heated while a mixture of acetone (100 cm³) and ethyl acetate (100 cm³) was added dropwise. The resultant fine crystals were digested at elevated temperature for several hours. After filtration and washing with ethyl acetate and ether the complexes were dried at 110 °C. Green crystals of Ni(ppda)₂(ClO₄)₂ and red Co(ppda)₂(ClO₄)₂·acet were obtained. Upon heating the latter complex to 230 °C, red Co(ppda)₂(ClO₄)₂ was produced. Green Ni(tpda)₂(ClO₄)₂ and blue Cu(ppda)₂(ClO₄)₂ were isolated in an analogous manner, the latter without the use of 2,2-dimethoxypropane.

Dioxane (10 cm³) was added to a hot, clear solution of anhydrous CoCl₂ (1.0 mmol) and tpda (1.0 mmol) dissolved in acetonitrile (35 cm³). The solution was boiled under reflux overnight, allowing some of the solvent to escape. Well-formed blue hygroscopic crystals of (CoCl₂)₃·2tpda were produced. Green, hygroscopic crystals of (NiCl₂)₃·2tpda were produced by refluxing a solution of anhydrous NiCl₂ (2 mmol) in a minimum of ethanol and tpda (1.5 mmol) in acetone (30 cm³) for several hours.

A solution of dpda (2.1 mmol) in dichloromethane (3 cm³) was added to a clear solution of anhydrous nickel bromide (2.0 mmol) in absolute alcohol (10 cm³). Cold ethyl acetate (20 cm³), followed by an excess of ether, was added dropwise to the stirred mixture. A fine green hygroscopic precipitate of αNiBr₂(dpda) was obtained. This complex could also be prepared by heating finely powdered NiBr₂(dpda)(dmp) to 120 °C.

An approximately 20% nickel bromide solution, which was prepared by dissolving 20 g nickel bromide trihydrate in 100 cm³ boiling absolute alcohol and 20 cm³ 2,2-dimethoxypropane, was used as starting material in the following preparations.

Nickel bromide (2.00 mmol) and dpda (2.1 mmol) dissolved in a mixture of ethanol (15 cm³) and 2,2-dimethoxypropane (10 cm³) was placed in a desiccator containing 100 cm³ ether. The desiccator was partially evacuated and left overnight. Well formed yellow green crystals of NiBr₂(dpda)(dmp) were obtained.

Ethyl acetate was added to a solution of nickel bromide (2 mmol) and dpda (2.1 mmol) dissolved in ethanol (15 cm³) until the first sign of turbidity. The resultant solution was gently heated to reflux, allowing some solvent to escape. After several hours red crystals of βNiBr₂(dpda) were formed. Red crystals of NiBr₂(dpda)(acet) were prepared in an analogous manner from a solution of nickel bromide and dpda dissolved in a mixture of ethanol (5 cm³) and acetone (25 cm³).

Analysis and Characterisation

Metal ions were analysed complexometrically and halide ions argentometrically using a Metrohm E536 potentiograph. Perchlorate was analysed gravimetrically using tetraphenylarsonium chloride as precipitant. Elemental C, H and N analyses were performed with a Heraeus rapid analyser. Infrared spectra were determined on a Beckman 4250 infrared spectrophotometer. Solution electronic spectra were measured using either a Beckman Acta MVII or a Perkin-Elmer 330 spectrophotometer, while solid reflectance spectra were measured on a Beckman DK2A spectrophotometer with a magnesium oxide integrating sphere. When necessary these spectra were resolved into gaussian components using non-linear least-squares techniques [6]. Differential scanning calorimetric and thermogravimetric analyses were performed with a Perkin-Elmer DSC2 differential scanning calorimeter and TG2 balance, respectively. Conductivity measurements were done using a Metrohm E365B conductoscope. Magnetic measurements were performed by the Gouy method, while powder X-ray diffraction was done using a Debye-Scherrer camera.

Analytical, conductivity and magnetic data are summarised in Table 1.

Crystal Structure Determination of βNiBr₂(dpda)

Crystal data: C₂₁H₁₉Br₂N₃NiO₂, *M_r* = 563.9, monoclinic, space group *P*2₁/*a*, *a* = 9.878, *b* = 16.029, *c* = 13.871 Å, β = 95.492°, *U* = 2186 Å³, *Z* = 4, *D_m* = 1.70, *D_c* = 1.71 g/cm³, μ(Mo Kα) = 46.4 cm⁻¹, λ = 0.7107 Å.

TABLE 1. Analytical, magnetic and conductivity data

| Complex | Metal (%) | | Anion (%) | | C (%) | | H (%) | | N (%) | | Magnetic moment (BM) | Conductivity ^a (S cm ² /mol) | |
|---|-----------|-------|-----------|-------|-------|-------|-------|-------|-------|-------|----------------------|--|-----------------|
| | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. | | Λ_{1000} | Λ_{500} |
| Ni(tpda) ₂ (ClO ₄) ₂ | 8.40 | 8.39 | 28.1 | 28.4 | 37.4 | 37.7 | 4.5 | 4.3 | 11.9 | 12.0 | 3.16 | 187 | 173 |
| Ni(ppda) ₂ (ClO ₄) ₂ | 6.23 | 6.35 | 20.9 | 21.5 | 49.5 | 49.4 | 6.8 | 6.8 | 8.9 | 9.1 | 3.25 | 197 | 186 |
| Co(pdpa) ₂ (ClO ₄) ₂ | 6.37 | 6.37 | 21.4 | 21.5 | 49.8 | 49.4 | 6.7 | 6.8 | 9.3 | 9.1 | 4.80 | 195 | 178 |
| Co(ppda) ₂ (ClO ₄) ₂ (acet) | 5.92 | 6.00 | 20.1 | 20.2 | 49.7 | 50.1 | 6.9 | 7.0 | 8.5 | 8.6 | 4.82 | | |
| Cu(ppda) ₂ (ClO ₄) ₂ | 6.98 | 6.84 | 21.4 | 21.4 | 48.9 | 49.1 | 6.7 | 6.7 | 9.3 | 9.6 | 1.97 | 193 | 179 |
| (CoCl ₂) ₃ (tpda) ₂ | 21.30 | 21.25 | 25.6 | 25.6 | 32.0 | 31.8 | 3.7 | 3.6 | 10.2 | 10.1 | 4.26 | | |
| (NiCl ₂) ₃ (tpda) ₂ | 21.20 | 21.19 | 25.6 | 25.6 | 31.7 | 31.8 | 3.8 | 3.6 | 9.9 | 10.1 | 3.40 | | |
| α NiBr ₂ (dpda) | 10.35 | 10.41 | 28.0 | 28.3 | 44.2 | 44.7 | 3.5 | 3.4 | 7.6 | 7.5 | 3.44 | 29 | 24 |
| NiBr ₂ (dpda)(dmp) | 8.83 | 8.79 | 23.8 | 23.9 | 46.3 | 46.8 | 4.7 | 4.7 | 6.5 | 6.3 | 3.41 | 32 | 25 |
| β NiBr ₂ (dpda) | 10.40 | 10.41 | 28.3 | 28.3 | 44.4 | 44.7 | 3.4 | 3.4 | 7.5 | 7.5 | 3.44 | 31 | 25 |
| NiBr ₂ (dpda)(acet) | 9.40 | 9.44 | 25.7 | 25.7 | 45.9 | 46.3 | 4.1 | 4.1 | 6.6 | 6.8 | 3.42 | 29 | 23 |

^a Λ_{1000} complex concentration = 0.001 mol/dm³; Λ_{500} complex concentration = 0.002 mol/dm³.

The space group and preliminary cell dimensions were obtained from Weissenberg and precession photographs using Cu K α radiation. Intensity data were collected using a parallelepiped crystal, of size 0.16 \times 0.20 \times 0.24 mm, on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo K α radiation. The ω - 2θ scan technique was used with the θ range being 3° to 22°, scan width of 0.4° and a scan speed of 0.02°/s. During data collection, the intensities of three standard reflections were measured every 50 reflections with no evidence of decomposition or crystal movement. Of the 2798 reflections, 2221 had $I > 2\sigma(I)$ and were used in the refinement. Accurate cell dimensions were obtained by least-squares refinement of 25 high order reflections.

The structure was solved using Patterson and Fourier techniques. The refinement was done via numerous stages of overlapping blocked matrices due to limited computer core size. The nickel, bromine, oxygen and methyl carbon atoms were refined anisotropically. Hydrogen atoms were introduced by placing them at theoretically calculated positions and allowed to ride on the adjacent carbon atoms during refinement. This led to convergence with $R = 0.0549$ and $R_w = 0.0580$ where $w = 1/(\sigma^2(F_o) + gF_o^2)$; g refined to 1.202×10^{-3} . The estimated standard deviations and magnitudes of the thermal parameters contained no anomalously high results. However, it must be noted that the standard deviations reported are somewhat underestimated since a blocked matrix method of refinement was used. All calculations were carried out with the SHELX-76 program system [7]. Anisotropic thermal parameters, hydrogen atoms positions and structure factor tables may be obtained from the authors. Fractional atomic coordinates of non-hydrogen atoms are listed in Table 2.

TABLE 2. Fractional atomic coordinates and isotropic thermal parameters for non-hydrogen atoms with standard deviations in parentheses

| Atom | x/a | y/b | z/c | U_{11} |
|------|------------|-----------|------------|------------|
| Ni | 0.6606(1) | 0.4322(1) | 0.0986(1) | 0.0345(6) |
| Br1 | 0.8096(1) | 0.3180(1) | 0.1503(1) | 0.0523(6) |
| Br2 | 0.6896(1) | 0.5450(1) | 0.2101(1) | 0.0513(6) |
| O1 | 0.4806(5) | 0.3759(4) | 0.1417(4) | 0.0428(32) |
| O2 | 0.7795(5) | 0.4794(4) | -0.0078(4) | 0.0430(32) |
| C2 | 0.7594(8) | 0.4448(5) | -0.0874(6) | 0.0372(19) |
| C8 | 0.4239(8) | 0.3277(5) | 0.0807(6) | 0.0368(19) |
| N1 | 0.5814(6) | 0.3749(3) | -0.0223(4) | 0.0305(14) |
| C3 | 0.6567(7) | 0.3737(5) | -0.0959(5) | 0.0349(18) |
| C4 | 0.6516(8) | 0.3081(5) | -0.1621(6) | 0.0421(21) |
| C5 | 0.5623(8) | 0.2441(5) | -0.1491(6) | 0.0430(20) |
| C6 | 0.4776(8) | 0.2463(5) | -0.0751(6) | 0.0382(19) |
| C7 | 0.4887(8) | 0.3142(5) | -0.0122(6) | 0.0373(19) |
| N3 | 0.8274(7) | 0.4664(4) | -0.1624(5) | 0.0397(16) |
| C1 | 0.9453(8) | 0.5227(6) | -0.1428(7) | 0.0282(45) |
| C10 | 0.7797(8) | 0.4499(5) | -0.2619(6) | 0.0381(19) |
| C11 | 0.8674(10) | 0.4126(6) | -0.3229(7) | 0.0562(24) |
| C12 | 0.8120(12) | 0.3965(7) | -0.4182(9) | 0.0817(33) |
| C13 | 0.6844(12) | 0.4184(7) | -0.4505(9) | 0.0802(33) |
| C14 | 0.6024(11) | 0.4562(7) | -0.3903(8) | 0.0725(30) |
| C15 | 0.6508(9) | 0.4736(5) | -0.2947(6) | 0.0480(22) |
| N2 | 0.3105(6) | 0.2859(4) | 0.0981(5) | 0.0378(16) |
| C9 | 0.2593(9) | 0.2912(6) | 0.1955(6) | 0.0461(52) |
| C16 | 0.2227(7) | 0.2428(5) | 0.0244(5) | 0.0352(19) |
| C17 | 0.2079(9) | 0.1570(6) | 0.0315(6) | 0.0498(22) |
| C18 | 0.1166(10) | 0.1175(7) | -0.0396(7) | 0.0676(28) |
| C19 | 0.0476(10) | 0.1626(6) | -0.1112(7) | 0.0651(27) |
| C20 | 0.0631(10) | 0.2471(6) | -0.1160(7) | 0.0624(26) |
| C21 | 0.1526(8) | 0.2884(5) | -0.0468(6) | 0.0442(21) |

Results and Discussion

The characterisation data for the complex M-(ppda)₂(ClO₄)₂, where M = Co, Ni and Cu, are

TABLE 3. Electronic and infrared spectral data with absorptivity coefficients in parentheses

| Complex | Medium | Electronic spectra (nm) | Infrared spectra (cm ⁻¹) | | | |
|---|---------------------------------|------------------------------------|--------------------------------------|--------------------|--------------|--------------------|
| | | | $\nu(\text{CO})$ | $\nu(\text{Cl-O})$ | pyr. def. | $\nu(\text{M-Cl})$ |
| Ni(tpda) ₂ (ClO ₄) ₂ | CH ₃ CN | 630(11), 1075(21) | 1615 | 1085(br) | 660, 680 | |
| Ni(ppda) ₂ (ClO ₄) ₂ | solid | 650, 1000(br) | 1600 | 1090(br) | 670 | |
| Co(ppda) ₂ (ClO ₄) ₂ | CH ₃ NO ₂ | 660(24), 1050(45) | 1600 | 1090(br) | 660, 665(sh) | |
| | solid | 490, 530, 1150 | | | | |
| Co(ppda) ₂ (ClO ₄) ₂ (acet) | CH ₃ NO ₂ | 505(100), 540(100), 1100(24) | 1600, 1745 | 1090(br) | 660 | |
| | solid | 500, 540, 590(sh), 1300(br) | | | | |
| Cu(ppda) ₂ (ClO ₄) ₂ | solid | 850(br) | 1600, 1640 | 1085, 1115 | 670, 678 | |
| | CH ₃ NO ₂ | 840(109), 1400(60) | | | | |
| (CoCl ₂) ₃ (tpda) ₂ | solid | 450, 490, 530, 605, 657, 1400–2000 | 1610 | | 675 | 320, 297 |
| (NiCl ₂) ₃ (tpda) ₂ | solid | 630, 715, 1250 | 1610 | | 675 | 310, 290 |
| α NiBr ₂ (dpda) | solid | 450(sh), 710, 1200(br) | 1610 | | 660, 678 | |
| NiBr ₂ (dpda)(dmp) | solid | 450(sh), 750, 1300(br) | 1610–1620 | | 660, 680 | |
| β NiBr ₂ (dpda) | solid | 505, 550(sh), 1000–1300 | 1610–1620 | | 660, 680 | |
| NiBr ₂ (dpda)(acet) | solid | 500, 550(sh), 1000–1300 | 1625, 1720 | | 670, 688 | |
| NiBr ₂ (dpda) | CH ₂ Cl ₂ | 505(121), 990(28) | | | | |
| | CH ₃ NO ₂ | 505(57), 590(45), 630(sh), 700(sh) | | | | |
| | | 1100(26) | | | | |
| tpda | | | 1640 | | 610–620 | |
| dpda | | | 1645 | | 610 | |
| ppda | | | 1640 | | 610 | |

sh = shoulder, br = broad.

ambiguous. The broad bands in the region 1080–1200 cm⁻¹, found in the infrared spectra (Table 3) are indicative of ionic perchlorate. This is in agreement with the conductivity data (Table 1) of the complexes in solution; these correspond to that of a 1:2 electrolyte [8]. The presence of a single $\nu(\text{CO})$ absorption band, shifted by 45 cm⁻¹ to lower energy when compared to the free ligands, in the infrared spectra of Co(ppda)₂(ClO₄)₂ and Ni(ppda)₂(ClO₄)₂ indicate that both carbonyl groups are coordinated in a similar manner. The absorption band at 670 cm⁻¹ is indicative of pyridine coordination [9]. Since the above data indicate that both ppda ligands are coordinated in a tridentate manner, the cobalt and nickel complexes must have octahedral coordination spheres. The energies of the absorption bands in the electronic spectra (Table 3) are consistent with this assignment. However, the absorptivity coefficients for these bands are high. An assignment of a highly distorted octahedral symmetry for the coordination spheres of [Co(ppda)₂](ClO₄)₂ and [Ni(ppda)₂](ClO₄)₂ is most consistent with the above data. The characterisation data of Cu(ppda)₂(ClO₄)₂ differs from that of the above complexes in that the infrared $\nu(\text{CO})$ band is split. This phenomenon was also observed in the complex Cu-Cl₂(ttda) where ttda is *N,N,N',N'*-tetramethylthioacetamide [1]. An X-ray structure determination indicated that the apical Cu–O bond was significantly longer than the basal Cu–O bond [10]. If a sim-

TABLE 4. Assignment of the spin allowed electronic transitions in the two chromophores of (MCl₂)₃(tpda)₂ in cm⁻¹

| | ⁴ T ₁ (F) ← ⁴ A ₂ | ⁴ T ₁ (P) ← ⁴ A ₂ |
|---------------------------------|---|---|
| CoCl ₄ ²⁻ | 4585, 5500 | 14660, 15610 |
| CoCl(tpda) ⁺ | 6910, 7250 | 13320, 13940, 17070, 18930 |
| | ³ A ₂ ← ³ T ₁ | ³ T ₁ (P) ← ³ T ₁ |
| NiCl ₄ ²⁻ | 7410 | 14160, 15330 |
| NiCl(tpda) ⁺ | 8530 | 12770, 13530, 16210, 17190 |

ilar explanation is applied to [Cu(ppda)₂](ClO₄)₂ the chromophore of this complex has tetragonally distorted octahedral symmetry. The high absorptivity coefficients and the large splitting of the $\nu(\text{CO})$ band, indicate this distortion to be pronounced. The distortions in the three complexes above can be attributed to the steric hindrance caused by the presence of bulky isopropyl groups near the carbonyl oxygen donor atoms. This conclusion is made because the characterisation data for [Ni(tpda)₂](ClO₄)₂ (Table 3) in which these bulky groups are absent, is consistent with the assignment of a more regular octahedral coordination sphere. This was also observed in the remaining [ML₂](ClO₄)₂, where M = Co, Ni and Cu, L = tpda and dpda, complexes [11]. The characterisation data for Co(ppda)₂(ClO₄)₂-

TABLE 5. Summary of some pertinent data obtained from non-isothermal thermogravimetric and differential scanning calorimetric curves

| Reaction | Temperature range (°C) | Loss (%) | | DSc (kJ/mol) |
|---|------------------------|----------|-------|--------------|
| | | exp. | calc. | |
| $[\text{Co}(\text{ppda})_2](\text{ClO}_4)_2(\text{acet})_{(s)} \rightarrow [\text{Co}(\text{ppda})_2](\text{ClO}_4)_{2(s)} + \text{acet}$ | 190–220 | 5.9 | 5.9 | 59 |
| $\text{NiBr}_2(\text{dpda})(\text{dmp})_{(s)} \rightarrow \alpha\text{NiBr}_2(\text{dpda})_{(s)} + \text{dmp}$ | 60–110 | 15.4 | 15.6 | 114 |
| $\text{NiBr}_2(\text{dpda})(\text{acet})_{(s)} \rightarrow \beta\text{NiBr}_2(\text{dpda})_{(s)} + \text{acet}$ | 200–220 | 9.2 | 9.3 | 74, -21, 8 |

(acet), where acet = acetone, is similar to that of $[\text{Co}(\text{ppda})_2](\text{ClO}_4)_2$. The acetone entity does not appear to be coordinated to the cobalt atom since the infrared $\nu(\text{CO})$ band for acetone is shifted to a slightly higher energy after complexation (coordination of a carbonyl group is usually associated with a decrease in energy) and the energy required to release it is low (Table 5). Therefore, a distorted octahedral coordination sphere, similar to that of $[\text{Co}(\text{ppda})_2](\text{ClO}_4)_2$, is assigned to $[\text{Co}(\text{ppda})_2](\text{ClO}_4)_2 \cdot \text{acet}$.

It has been shown that the addition of tpda to copper chloride results in the formation of the crystalline pentacoordinate complex $\text{CuCl}_2(\text{tpda})$ [3]. Impure $\text{MCl}_2(\text{tpda})$, $\text{M} = \text{Co}$ and Ni , can be isolated at room temperature in powder form [11]. However, crystallisation from hot solutions results in $(\text{MCl}_2)_3(\text{tpda})_2$. Powder X-ray diffraction shows the two complexes to be isostructural. Interpretation of the characterisation data for these complex compounds proved difficult since the dominant species present in a solution are not necessarily crystallised in the solid state. Therefore, solution characterisation data cannot be used. The infrared spectra contains single $\nu(\text{CO})$ bands (Table 3) thus indicating similar coordination of the two carbonyl groups. The regions of the spectra in which $\nu(\text{M}-\text{Cl})$ vibrations are expected each contains two bands. The bands at 290 and 297 cm^{-1} for the spectra of $(\text{NiCl}_2)_3(\text{tpda})_2$ and $(\text{CoCl}_2)_3(\text{tpda})_2$ respectively, correlate closely to the bands found in the spectrum of NiCl_4^{2-} and CoCl_4^{2-} complexes [9]. The second $\nu(\text{M}-\text{Cl})$ vibration is found at approximately 20 cm^{-1} higher energy thus indicating different $\text{M}-\text{Cl}$ bonds. These spectra are therefore consistent with the assignment $[\text{MCl}(\text{tpda})]_2[\text{MCl}_4]$. The magnitudes of the magnetic moments of both complexes (Table 1) fall in the range expected for tetrahedral complexes. However, the magnetic moments for CoCl_4^{2-} and NiCl_4^{2-} which are 4.70 and 3.89 BM respectively, are significantly higher than for the $[\text{MCl}(\text{tpda})]_2[\text{MCl}_4]$ complexes. These values can readily be rationalised by the lower symmetry of the two $\text{MCl}(\text{tpda})^+$ moieties present in these complexes; a decrease in symmetry causes the magnetic moment to decrease towards the spin only value. Further-

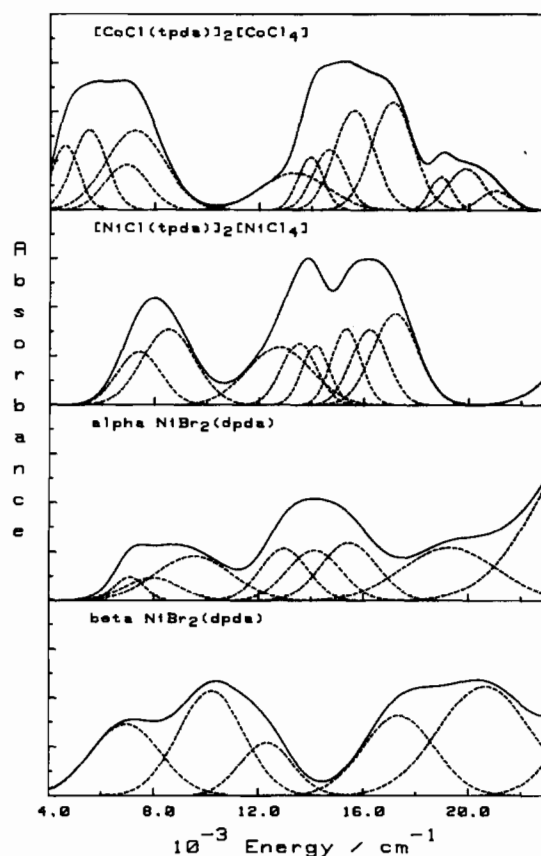


Fig. 1. The solid reflectance electronic spectra of the four complexes resolved into gaussian components.

more, the ligand fields for the $\text{MCl}(\text{tpda})^+$ moieties are greater than that of MCl_4^{2-} . This also contributes towards lowering of the magnetic moment of divalent nickel ions having T ground states [12]. It is obvious that the presence of two distinctly different chromophores in a single compound will lead to complex solid reflectance electronic spectra for $(\text{MCl}_2)_3(\text{tpda})_2$. These spectra were successfully resolved into gaussian components, Fig. 1.

The positions of the bands for the MCl_4^{2-} moieties can be obtained from the literature [13] and can therefore be identified (Table 4). In the spectrum of $(\text{NiCl}_2)_3(\text{tpda})_2$ two bands attributed

to the ${}^3A_2 \leftarrow {}^3T_1$ transition are found at 7410 and 8530 cm^{-1} . Since the literature value for this transition in NiCl_4^{2-} is 7407 cm^{-1} , the first band is ascribed to this moiety and the second to $\text{NiCl}(\text{tpda})^+$. This is in accordance with the higher ligand field caused by a pyridine nitrogen and two carboxamide oxygen donor atoms compared to chlorine donor atoms. The existence of only two absorption bands is in agreement with an A excited state; a decrease in symmetry does not affect a unidimensional term. Although the ${}^3T_1(\text{P}) \leftarrow {}^3T_1$ transition is already split in NiCl_4^{2-} , the lower symmetry inherent in $\text{NiCl}(\text{tpda})^+$ causes further splitting. These components are at both lower and higher energy than the transitions for NiCl_4^{2-} . However, the baricentre of these bands is at a higher energy than the baricentre of the NiCl_4^{2-} bands. The spectrum of $(\text{CoCl}_2)_3(\text{tpda})_2$ can be interpreted in an analogous manner and provides sound evidence for the presence of both $\text{CoCl}(\text{tpda})^+$ and CoCl_4^{2-} moieties. Furthermore, the characteristic doublet transitions found on the high energy side of the ${}^4T_1(\text{P}) \leftarrow {}^4A_2$ transitions in some tetrahedral cobalt complexes can also be identified (Fig. 1).

The above characterisation data provides concrete evidence for the assignment of cations, having distorted tetrahedral chromophores, and anions, which are tetrahedral, to the $(\text{MCl}_2)_3(\text{tpda})_2$ complexes. At room temperature the species which predominates in solution, when equimolar amounts of MCl_2 and tpda are added, is pentacoordinate $\text{MCl}_2(\text{tpda})$. It is expected that an increase in temperature causes an increase in the $\text{MCl}(\text{tpda})^+$ concentration. However, the driving force for the formation of the $[\text{MCl}(\text{tpda})]_2[\text{MCl}_4]$ complexes is probably the stabilisation energy associated with the presence of a doubly charged anion in an ionic lattice. The analogous complexes of dpda and ppda could not be isolated.

The infrared spectrum of $\alpha\text{NiBr}_2(\text{dpda})$ contains a relatively symmetrical $\nu(\text{CO})$ absorption at 1610 cm^{-1} . The decrease in energy of 35 cm^{-1} and the presence of only a single band indicates that both the carbonyl oxygen atoms are bonded to the nickel in a similar manner. The coordination of the pyridine nitrogen atom is confirmed by the splitting of the ring deformation absorption into two bands at 660 and 678 cm^{-1} . The $\nu(\text{Ni}-\text{Br})$ frequency usually occurs below 300 cm^{-1} and could not be identified. However, the relatively low conductivity of solutions of this complex in nitromethane indicates the coordination of both bromine atoms. Although this data suggests a pentacoordinated nickel atom, an octahedral coordination sphere could be attained by either metal-metal interaction or by bridging via an oxygen atom or, more likely, a bromine atom. The magnetic moment of 3.44 BM is consistent with pentacoordinate nickel and furthermore eliminates the possibility of a nickel-nickel bond. Bridging via

a single carbonyl oxygen atom can be disregarded since it would have resulted in a split $\nu(\text{CO})$ absorption band. Bromine bridging is also unlikely, since the coordination of the tridentate dpda ligand to a NiBr_3 entity would be highly improbable for steric reasons.

Electronic spectra of solutions of the chromophore in $\alpha\text{NiBr}_2(\text{dpda})$ could not be obtained. The spectrum of $\alpha\text{NiBr}_2(\text{dpda})$ dissolved in dichloromethane corresponds closely to the solid reflectance spectrum of $\beta\text{NiBr}_2(\text{dpda})$. Although a solution of $\text{NiBr}_2(\text{dpda})$ in nitromethane appears to contain a mixture of the two species, the extinction coefficients for the absorption bands in this spectrum are in excess of those normally associated with octahedral chromophores. The above reasoning, as well as the fact that the solid reflectance spectrum (Fig. 1) of $\alpha\text{NiBr}_2(\text{dpda})$ is typical of that for a pentacoordinate complex [1, 14], allows the assignment of a pentacoordinate coordination sphere to be made with confidence.

The exact stereochemistry of the coordination sphere of $\alpha\text{NiBr}_2(\text{dpda})$ could not be determined since the compound could only be isolated in powder form thus making a single crystal structure determination impossible. However, the crystalline complex $\text{NiBr}_2(\text{dpda})(\text{dmp})$ was isolated. Its characterisation data is similar to that of $\alpha\text{NiBr}_2(\text{dpda})$. This indicates the coordination of both carbonyl oxygen atoms and the pyridine nitrogen atom of dpda , as well as the coordination of the two bromine atoms. It is unlikely that the 2,2-dimethoxypropane molecule is coordinated to the nickel since it only contains two weakly coordinating ethereal oxygen atoms. Furthermore, the 2,2-dimethoxypropane is readily removed by heating (Table 5); the loss being more time dependent than temperature dependent. There is little change in the solid reflectance electronic spectra, the infrared spectra and the magnetic moments upon formation of $\alpha\text{NiBr}_2(\text{dpda})$ by heating $\text{NiBr}_2(\text{dpda})(\text{dmp})$. This indicates similar pentacoordinate chromophores in both complexes. An X-ray structure analysis was attempted on the latter crystalline compound (space group $P222_1$, orthorhombic $a = 12.673(16)$, $b = 16.527(8)$, $c = 13.355(7)$ Å), but the compound was unstable and all attempts failed.

The infrared spectrum of red $\beta\text{NiBr}_2(\text{dpda})$ confirms the coordination of all three donor atoms in dpda while the conductivity data indicates bromine coordination. The electronic spectra, both solid reflectance (Fig. 1) and from dichloromethane solution, are unlike those of other nickel(II) ions in pentacoordinate environments and are more consistent with spectra of square planar nickel complexes. The spectra of square planar complexes typically contain two bands in the near infrared and visible regions but at higher energy than bands

for pentacoordinate complexes with similar donor atoms. If one of the bromine atoms in $\beta\text{NiBr}_2(\text{dpda})$ is ionically bonded then the complex could have a distorted square planar chromophore. The fact that the conductivity of $\beta\text{NiBr}_2(\text{dpda})$ when measured in dichloromethane solution was very low ($\Lambda_{1000} = 2 \text{ S cm}^2/\text{mol}$), could be rationalised by ion pair formation which is likely to occur in such non-polar solvents. The conductivity, when measured in the more polar nitromethane solution, is sufficiently large to account for the ionisation of one bromine atom if it is assumed that only part of the $\text{NiBr}_2(\text{dpda})$ is in the beta form. Furthermore, the only significant difference between the preparation methods of $\alpha\text{NiBr}_2(\text{dpda})$ and $\beta\text{NiBr}_2(\text{dpda})$ was that the latter was performed at a higher temperature; this favours the formations of a complex with a lower coordination number. Although there is considerable circumstantial evidence for the assignment of a square planar symmetry to $\beta\text{NiBr}_2(\text{dpda})$ this is inconsistent with its high magnetic moment. Square planar nickel(II) complexes are usually diamagnetic while this complex is paramagnetic with a magnetic moment similar to that of $\alpha\text{NiBr}_2(\text{dpda})$. A single crystal X-ray analysis was performed in order to determine the structure unequivocally.

The compound crystallised in a monoclinic $P2_1/a$ and an orthorhombic $Pbca$ space group. The structure determination was performed on crystals having the $P2_1/a$ space group.

The molecular configuration of $\beta\text{NiBr}_2(\text{dpda})$ is illustrated in Fig. 2 while selected bond lengths and angles are listed in Table 6. The structure of the molecule can best be described as a distorted square pyramid bisected by a mirror plane containing Ni, Br1, Br2, N1 and C5. The O1, N1 and O2 atoms of dpda and the Br2 form the basal plane, while Br1 occupies the apical position. The least-squares equation for this plane and the deviations of the constituent atoms are given in Table 7. The nickel atom is situated 0.385 Å above the basal plane.

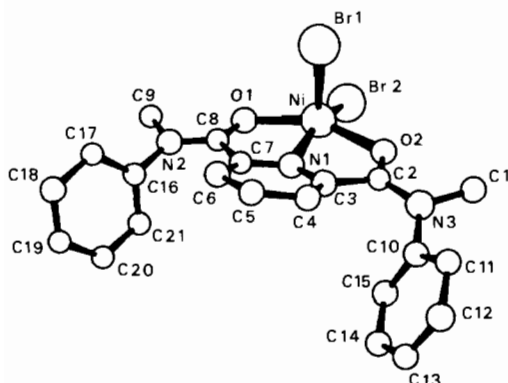


Fig. 2. A perspective view and atomic numbering scheme of $\beta\text{NiBr}_2(\text{dpda})$.

TABLE 6. Selected interatomic distances (Å) and angles (°) with standard deviations in parentheses

| Bonds | | Angles | |
|---------|-----------|-------------|-----------|
| Ni-Br1 | 2.415(1) | Br1-Ni-Br2 | 110.6(0) |
| Ni-Br2 | 2.378(1) | Br1-Ni-O1 | 95.6(2) |
| Ni-O1 | 2.131(5) | Br2-Ni-O1 | 101.0(1) |
| Ni-O2 | 2.112(5) | Br1-Ni-O2 | 96.6(2) |
| Ni-N1 | 2.005(6) | Br1-Ni-N1 | 94.5(2) |
| | | Br2-Ni-O2 | 98.2(2) |
| O1-C8 | 1.239(9) | N1-Ni-O1 | 76.8(2) |
| O2-C2 | 1.235(9) | N1-Ni-O2 | 77.2(2) |
| C7-C8 | 1.508(11) | | |
| C2-C3 | 1.522(11) | O1-C8-N2 | 121.1(7) |
| N2-C8 | 1.346(10) | O1-C8-C7 | 118.1(7) |
| N2-C9 | 1.490(11) | O2-C2-C3 | 122.0(7) |
| N2-C16 | 1.451(10) | O2-C2-C3 | 117.0(7) |
| N3-C2 | 1.336(10) | C8-N2-C9 | 119.6(7) |
| N3-C1 | 1.478(10) | C8-N2-C16 | 124.2(7) |
| N3-C10 | 1.439(10) | C9-N2-C16 | 115.7(6) |
| | | C2-N3-C1 | 117.5(7) |
| N1-C3 | 1.319(9) | C2-N3-C10 | 123.7(7) |
| N1-C7 | 1.352(9) | C1-N3-C10 | 117.9(7) |
| C3-C4 | 1.395(11) | | |
| C6-C7 | 1.392(11) | C3-N1-C7 | 120.5(6) |
| C4-C5 | 1.376(11) | N1-C3-C4 | 122.2(7) |
| C5-C6 | 1.386(11) | N1-C7-C6 | 120.7(7) |
| | | C5-C6-C7 | 117.9(7) |
| C16-C17 | 1.388(12) | C4-C5-C6 | 121.1(8) |
| C16-C21 | 1.363(11) | C3-C4-C5 | 121.3(4) |
| C17-C18 | 1.420(12) | | |
| C20-C21 | 1.407(12) | C17-C16-C21 | 122.2(8) |
| C18-C19 | 1.358(13) | C16-C17-C18 | 117.2(8) |
| C19-C20 | 1.366(14) | C16-C21-C20 | 119.0(8) |
| | | C17-C18-C19 | 120.8(10) |
| C10-C11 | 1.402(12) | C21-C20-C19 | 119.9(9) |
| C10-C15 | 1.365(11) | C18-C19-C20 | 120.9(10) |
| C11-C12 | 1.405(14) | | |
| C14-C15 | 1.394(13) | C11-C10-C15 | 121.8(8) |
| C12-C13 | 1.344(15) | C10-C11-C12 | 116.0(9) |
| C13-C14 | 1.359(15) | C10-C15-C14 | 119.1(9) |
| | | C11-C12-C13 | 122.3(11) |
| | | C13-C14-C15 | 120.2(10) |
| | | C12-C13-C14 | 120.4(12) |

TABLE 7. The details of the least-squares calculated basal plane for $\beta\text{NiBr}_2(\text{dpda})$

| Atoms | Deviations from the plane (Å) |
|-------|-------------------------------|
| Br2 | -0.0607 |
| O1 | 0.0841 |
| O2 | 0.0862 |
| N1 | -0.1096 |

Equation of the plane: $6.1653x - 10.5126y + 5.0343z = -0.3594$.

Such a deviation is energetically favourable and this phenomenon is observed in most square pyramidal complexes. This has considerable significance since the four basal atoms effectively restrict the approach of a ligand to the sixth coordination site. The apical Ni–Br1 bond length of 2.415 Å is significantly longer than the basal Ni–Br2 bond length of 2.377 Å. Similar distortions are evident in the analogous compounds CuCl₂(tpda) [3] and βCoBr₂(tpda) [4]. The Ni–O1 and Ni–O2 bond lengths are very similar, namely 2.131 and 2.112 Å respectively, indicating similar carbonyl oxygen coordination. The bond angles involving the amide nitrogen atoms as centres are all approximately 120°; indicating a large degree of sp² hybridisation at these centres. This can readily be rationalised by assuming delocalisation of the lone pair of electrons on each nitrogen towards the coordinating carbonyl groups. The resultant double bond character between the nitrogen and the carbonyl carbon atoms is reflected in the short N–C (carbonyl) bond lengths, viz. N2–C8 = 1.346 Å and N3–C2 = 1.336 Å. The small O1–Ni–N1 and O2–Ni–N1 bond angles of 76.8° and 77.3° respectively are indicative of the restrictions which the rigid nature of the ligand places on the donor atoms. This rigidity would make the coordination of a carbonyl oxygen from the apical position, as found in other tridentate dicarboxylamide ligands [10], unlikely. Although a trigonal bipyramidal symmetry is theoretically more stable than a square pyramidal symmetry [15], it can readily be seen that such coordination would be impossible due to the restrictions inherent in the ligand.

During attempts to obtain βNiBr₂(dpda) in crystalline form, the complex NiBr₂(dpda)(acet) was isolated. The characterisation data indicates coordination of dpda and the two bromine atoms in the usual manner. The acetone molecule is strongly bound and is lost when the complex melts at 220 °C (Table 5). The ν(CO)(acetone) absorption band in the complex is in a similar position to that in pure acetone, thus showing non-coordination of this carbonyl group. Since the electronic spectra of

βNiBr₂(dpda) and NiBr₂(dpda)(acet) are almost identical, the latter must also contain a pentacoordinate distorted square pyramidal nickel chromophore.

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