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# Metal Compounds of Tetra-amines with Terminal Pyridyl Residues. Crystal and Molecular Structures of $[M(C_{15}H_{20}N_4)](ClO_4)_2$ {M = Pd, Cu}

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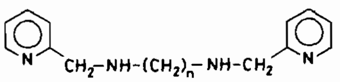
*Single crystal X-ray analyses of 1,7-bis(2-pyridyl)-2,6-diazaheptanecopper(II) perchlorate and -palladium(II) perchlorate have been carried out. Both compounds crystallise in orthorhombic unit cells with Z = 8: for the Cu compound, space group* Pnma *with dimensions* a = *13.746(1),* b = *26.388(2),* c = *11.225(1) Å; and for the Pd compound, space group* Pmn2₁ *(only 39 weak reflections break the condition* k ≠ *2n for* hk0*, which would allow the same space group as the Cu analogue) with dimensions* a = *26.97(1),* b = *13.81(1),* c = *10.90(1) Å. The structures were solved by the heavy atom method and refined by least-squares techniques to* R = *0.109 for 925 unique diffractometer data for the Cu compound and to* R = *0.101 for 2190 unique photographic data for the Pd analogue. All atoms were placed in the Pd structure, but the Cu structure showed disorder in position and occupancy of many perchlorate oxygen sites, and a smaller averaged disorder in the positions of some of the atoms in the cations. The* $[MN_4]$ *polyhedra are essentially planar, but with some tetrahedral twist and a twist-boat conformation in the trimethylene chelate rings – both of which are a response to the steric preferences of the amine ligand. Perchlorate oxygens approach the metals in axial (tetragonal) sites; between 2.93 and 3.23 Å for Pd, but closer at 2.64 and 2.70 Å for Cu. Differences in the i.r. spectra in the* $\nu_{N-H}$ *region appear now to result from the observed proximities of perchlorate oxygens to the N–H groups. However, there is no evidence for any water in a regular pattern in the crystals, which could account for i.r. bands observed at 3620 and 3540* $cm^{-1}$.

## Introduction

In our studies [1–3] of some metal compounds of the $[N_4]$ ligands I, we found [1] a number of crystalline species which had, in their i.r. spectra, two prominent bands at ~3600 $cm^{-1}$. Such bands, which were reproducible on different instruments, are typical of 'free' (non-H-bonded) water molecules. However, deuteriation experiments [1] seemed to deny this attribution: when recrystallised from $D_2O$, the N–H bands at ~3200 $cm^{-1}$ moved to lower energy, but the 3600 $cm^{-1}$ bands remained unchanged.



I

To prove the absence of water in these crystalline compounds, we have undertaken X-ray structural analyses first of $[Pd(bispictn)](ClO_4)_2$ (bispictn = I for n = 3), and later, because of space group and disorder problems encountered, of the almost isomorphous copper analogue.

Of interest also [1] was the conformation adopted by the quadridentate ligand.

## Experimental

### *The Palladium Compound*

Pale yellow prisms were obtained [1] by slow evaporation from an aqueous solution at 15–20 °C. If the solution was cooled in a refrigerator, transparent needles were formed. These became opaque when warmed to room temperature and presumably represent a different crystalline form – stable only at lower temperatures.

*Crystal data*: $C_{15}H_{20}N_4O_8Cl_2Pd$, M = 561.7, orthorhombic, $a$ = 26.97(1), $b$ = 13.81(1), $c$ = 10.90(1) Å, $U$ = 4059 Å$^3$, $D_m$ = 1.84 g cm$^{-3}$ (by flotation), $Z$ = 8, $D_c$ = 1.838 g cm$^{-3}$, $F(000)$ = 2256, $\mu(\text{Mo-}K_\alpha)$ = 12.1 $cm^{-1}$. Systematic absences $h0l$ if $h + l \neq 2n$, space group $Pmn2_1$ (No. 31) or $Pmnm$ (non-standard, No. 59).

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For the reflections $hk0$ there is a close approach to the systematic absence for $k \neq 2n$; only 39 weak reflections were observed to break this condition. Hence the space group approximates to $P2_1nb$ (non-standard, No. 33) or $Pmnb$ (non-standard, No. 62) – see copper analogue.

The crystal used for data collection had dimensions 0.60 × 0.25 × 0.13 mm. Cell parameters were determined from precession photographs using Mo-$K_\alpha$ radiation. Intensities were estimated visually from precession photographs for the layers 0–5 about [010] and 0–12 about [100]. They were corrected for Lorentz and polarisation effects but not for absorption or extinction. The structure factors were placed on a common scale by internal correlation and 2190 non-zero unique reflections obtained.

A three-dimensional Patterson synthesis indicated the non-centric space group $Pmn2_1$. The structure was solved by the heavy atom method. Refinement was by a least-squares method in which $\Sigma w\Delta^2$ was minimised. Initially $w$ was unity, but for the final cycles $w = (10.0 + 0.25\,|F_o| + 0.005\,|F_o|^2)^{-1}$. Refinement was in four matrices: (i) for the overall thermal and scale parameters; (ii) for the two independent molecular cations; (iii) for the two perchlorate ions in general positions; and (iv) the perchlorate ions on the mirror planes. Only the Pd atoms and the Cl atoms in general positions were allowed to vibrate anisotropically. Refinement was terminated when the maximum shift in any parameter was $<0.25\sigma$. The final value for $R$ was 0.101 and for $R'[=(\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}]$ was 0.135.

A final difference map showed peaks of absolute density to 2eÅ$^{-3}$ associated with the Pd atoms, but elsewhere only peaks of absolute density to 1 eÅ$^{-3}$ were observed. None of these peaks could reasonably be assigned to water molecules.

### *The Copper Compound*

*Crystal data*: $C_{15}H_{20}N_4O_8Cl_2Cu$, $M$ = 518.8, orthorhombic, $a$ = 13.746(1), $b$ = 26.388(2), $c$ = 11.225(1) Å, $u$ = 4071.6 Å$^3$, $D_m$ = 1.69 g cm$^{-3}$ (by flotation), $Z$ = 8, $D_c$ = 1.692 g cm$^{-3}$, $F(000)$ = 2120, $\mu$(Mo-$K_\alpha$) = 14.3 cm$^{-1}$. Systematic absences $0kl$ if $k + l \neq 2n$, $hk0$ if $h \neq 2n$, space group $Pn2_1a$ (non-standard, No. 33) or $Pnma$ (No. 62).

Blue-violet needles of the compound were obtained from aqueous solution. A short fragment of dimensions ~0.3 × 0.2 × 0.15 mm was used for the data collection. Data were collected on a Stöe four-circle diffractometer by Stöe A.G., Darmstadt using Mo-$K_\alpha$ radiation. Cell parameters were determined from a least-squares procedure using diffractometer measurements. The intensities were corrected for Lorentz and polarisation effects but not for absorption or extinction and a data set of 925 unique reflections obtained.

A three-dimensional Patterson synthesis indicated the centric space group $Pnma$ and this was confirmed by the successful analysis. The structure was solved by the heavy atom method. A difference synthesis phased by the molecular cation, Cl(1), Cl(2), O(11) and O(21) indicated disorder in the perchlorate groups. This was accounted for on an *ad hoc* basis by using a series of difference maps to adjust the occupancy of the observed sites for the atoms of the disorder anions.

Refinement was by a full-matrix least-squares procedure in which $\Sigma w\Delta^2$ was minimised. Initially $w$ was unity but for the final cycles $w = (50.0 + 0.3|F_o| + 0.002\,|F_o|^2)^{-1}$. Only the parameters for the molecular cation, Cl(1), Cl(2), O(11) and O(21) were refined. At the completion of isotropic refinement a difference map was calculated and approximate positions for fifteen of the twenty H atoms were indicated. These positions were optimised, assuming C–H to be 1.0 Å, and the contributions for these atoms included in subsequent calculations. Refinement was continued with anisotropic thermal parameters for Cu, Cl(1) and Cl(2) atoms only and was terminated when the maximum shift in any parameter was $<0.5\sigma$. The final value for $R$ was 0.109 and for $R'$, was 0.140. A final difference map showed no unusual features and no peak of density $>|1.3|$eÅ$^{-3}$.

Atomic scattering factors for both structures were taken from ref. 4. Calculations were carried out on the Macquarie University UNIVAC 1106 computer with programmes written by F.S.S.

The final atomic parameters are given in Table I. Observed structure amplitudes and calculated structure factors are in Tables which are available from the Editor.

## Results and Discussion

The structural analyses show the expected molecular cations and perchlorate anions, but reveal no evidence for any water molecules, in even partial occupancy. Figure 1 shows the numbering system used for both the Pd and Cu cations. Figure 2 gives a view of the Cu cation, showing the conformation of the amine ligand [1], and the positions of the perchlorates with respect to the metal cation. Bond lengths and angles, within the molecular ions, are listed in Table II and some least-squares planes are in Table III.

The two structures are closely related. For the Pd compound only 39 weak reflections in the zone $hk0$ where $k \neq 2n$ are observed, hence there is almost a $b$-glide plane perpendicular to $c$ and its presence would make the space groups identical to those for the Cu analogue. The two structures differ in detail exemplified by the following three features:

TABLE I. Final Atomic Parameters (fractional coordinates $\times 10^3$). Estimated standard deviations are given in parentheses. The anisotropic thermal parameters ($\times 10^4$) are in the form $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})]$.

(a) *Pd compound*

| | n = 1 | | | | n = 2 | | | |
|---|---|---|---|---|---|---|---|---|
| | *x/a* | *y/b* | *z/c* | $B$ (A$^2$) | *x/a* | *y/b* | *z/c* | $B$ (A$^2$) |
| Pd(n) | 133.2(1) | 23.9(3) | 58.2 | – | 363.2(1) | 476.2(3) | –59.8(3) | – |
| N(n1) | 168(1) | –101(3) | 116(4) | 3.7(8) | 332(1) | 599(2) | –111(3) | 2.1(6) |
| N(n2) | 149(1) | –36(2) | –107(3) | 2.5(5) | 344(1) | 523(2) | 113(3) | 3.1(6) |
| N(n3) | 102(1) | 147(2) | –12(3) | 3.3(7) | 394(2) | 351(3) | 8(5) | 5.6(12) |
| N(n4) | 112(1) | 82(3) | 214(4) | 3.4(7) | 391(1) | 419(3) | –224(4) | 3.5(7) |
| C(n1) | 191(1) | –119(2) | 224(4) | 2.4(6) | 313(2) | 625(3) | –211(5) | 4.2(10) |
| C(n2) | 214(1) | –209(3) | 247(4) | 2.9(7) | 292(2) | 709(4) | –236(4) | 3.9(9) |
| C(n3) | 212(1) | –273(2) | 162(3) | 3.0(6) | 292(1) | 793(2) | –143(3) | 2.9(6) |
| C(n4) | 189(1) | –264(2) | 29(4) | 3.0(7) | 310(2) | 758(3) | –56(5) | 4.1(8) |
| C(n5) | 171(1) | –173(3) | 26(4) | 2.9(8) | 331(1) | 667(3) | –19(4) | 3.3(9) |
| C(n6) | 150(1) | –144(2) | –99(3) | 2.4(6) | 358(2) | 630(3) | 101(5) | 5.0(11) |
| C(n7) | 123(1) | 12(3) | –212(4) | 3.2(8) | 382(2) | 495(4) | 196(6) | 6.4(15) |
| C(n8) | 117(3) | 111(6) | –225(8) | 9.8(20) | 372(1) | 385(3) | 229(4) | 4.2(8) |
| C(n9) | 124(2) | 183(4) | –116(5) | 4.8(11) | 377(2) | 328(4) | 129(6) | 5.3(12) |
| C(n10) | 99(1) | 214(3) | 74(4) | 4.4(8) | 398(1) | 275(3) | –99(4) | 4.3(9) |
| C(n11) | 96(1) | 180(3) | 213(4) | 3.1(7) | 407(2) | 335(3) | –207(4) | 3.3(8) |
| C(n12) | 69(2) | 218(4) | 315(5) | 4.5(10) | 426(2) | 276(3) | –291(4) | 4.1(9) |
| C(n13) | 65(2) | 174(4) | 407(6) | 6.0(13) | 437(2) | 331(3) | –414(5) | 4.9(11) |
| C(n14) | 80(1) | 70(4) | 439(5) | 4.9(9) | 424(1) | 420(3) | –414(4) | 3.7(7) |
| C(n15) | 101(1) | 32(3) | 322(4) | 3.1(7) | 399(2) | 464(4) | –330(7) | 6.7(15) |
| Cl(n1) | 222.9(3) | 432.8(8) | –59.0(15) | – | 278.4(3) | 64.9(7) | 52.5(14) | – |
| O(n11) | 230(1) | 463(2) | –177(4) | 6.1(7) | 275(2) | 43(4) | 189(7) | 13.0(16) |
| O(n12) | 227(1) | 509(3) | 14(4) | 8.3(11) | 265(2) | –15(4) | –23(5) | 9.8(13) |
| O(n13) | 260(1) | 372(3) | –8(5) | 9.8(12) | 238(2) | 135(3) | 30(6) | 11.5(15) |
| O(n14) | 174(1) | 396(3) | –27(4) | 6.9(9) | 323(1) | 112(3) | 39(5) | 7.7(9) |
| Cl(n2) | 0 | 468(1) | 455(1) | 4.2(2) | 0 | –49(1) | 72(1) | 3.5(2) |
| O(n21) | 45(1) | 410(2) | 449(3) | 5.3(6) | 42(1) | –99(2) | 13(3) | 4.8(6) |
| O(n22) | 0 | 530(4) | 361(5) | 8.5(13) | 0 | –58(3) | 195(5) | 7.3(11) |
| O(n23) | 0 | 525(3) | 553(5) | 7.2(10) | 0 | 55(3) | 31(4) | 5.6(8) |
| Cl(n3) | 0 | 324(1) | –162(2) | 7.2(4) | 0 | –201(2) | 712(3) | 10.8(7) |
| O(n31) | 41(2) | 377(3) | –130(4) | 9.9(7) | 46(3) | –157(5) | 748(7) | 17.7(21) |
| O(n32) | 0 | 239(2) | –91(3) | 4.4(7) | 0 | –139(3) | 590(4) | 5.9(9) |
| O(n33) | 0 | 287(5) | –298(7) | 16.6(20) | 0 | –294(7) | 642(12) | 17.7(32) |

| | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |
|---|---|---|---|---|---|---|
| Pd(1) | 11.1(4) | 41.0(20) | 72.5(39) | –1.6(7) | –1.1(14) | –2.3(23) |
| Pd(2) | 10.8(4) | 41.9(20) | 69.7(38) | 3.7(7) | –0.3(13) | 6.9(23) |
| Cl(11) | 12(1) | 53(7) | 98(13) | –4(2) | 6(5) | 9(8) |
| Cl(21) | 14(1) | 44(6) | 77(11) | 9(2) | –1(5) | –14(7) |

(b) *Cu compound*

| | *x/a* | *y/b* | *z/c* | $B$(A$^2$) |
|---|---|---|---|---|
| Cu | 239.9(2) | 383.6(2) | 49.2(3) | – |
| N(1) | 364(2) | 419(1) | 99(2) | 3.6(5) |
| N(2) | 301(2) | 388(2) | –113(3) | 7.2(8) |
| N(3) | 110(2) | 361(1) | –18(3) | 7.7(9) |
| N(4) | 184(2) | 359(1) | 205(2) | 3.2(5) |
| C(1) | 382(2) | 441(1) | 205(3) | 4.2(7) |
| C(2) | 473(2) | 465(1) | 228(3) | 3.0(6) |
| C(3) | 544(2) | 462(1) | 145(3) | 4.4(7) |

*(continued overleaf)*

TABLE I. *(continued)*

| | $x/a$ | $y/b$ | $z/c$ | $B$ (A$^2$) |
|---|---|---|---|---|
| C(4) | 524(2) | 437(1) | 32(3) | 3.1(6) |
| C(5) | 434(2) | 415(1) | 15(3) | 3.3(6) |
| C(6) | 404(2) | 389(1) | −104(3) | 5.6(8) |
| C(7) | 260(3) | 371(2) | −215(4) | 8.5(12) |
| C(8) | 155(3) | 370(1) | −227(3) | 5.7(9) |
| C(9) | 85(3) | 369(2) | −132(4) | 7.8(11) |
| C(10) | 42(2) | 357(1) | 79(3) | 4.1(7) |
| C(11) | 87(2) | 348(1) | 195(3) | 3.0(6) |
| C(12) | 42(2) | 324(1) | 296(3) | 3.9(7) |
| C(13) | 93(2) | 315(1) | 390(3) | 3.6(7) |
| C(14) | 186(2) | 328(1) | 404(3) | 4.7(8) |
| C(15) | 230(2) | 351(1) | 309(3) | 3.6(6) |
| Cl(1) | 177.8(5) | 518.9(3) | 47.6(10) | – |
| Cl(2) | 292.4(10) | 250 | 68.8(16) | – |
| O(11) | 158(2) | 473(1) | 80(3) | 9.8(9) |
| O(21) | 340(2) | 295(1) | 51(3) | 8.7(7) |

| | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |
|---|---|---|---|---|---|---|
| Cu | 29(2) | 20(1) | 62(3) | −6(1) | −3(3) | −2(2) |
| Cl(1) | 51(5) | 12(2) | 152(11) | −6(2) | −8(7) | 13(4) |
| Cl(2) | 84(9) | 11(2) | 180(21) | 0 | 17(12) | 0 |

| | $x/a$ | $y/b$ | $z/c$ | occupancy |
|---|---|---|---|---|
| O(12) | 99 | 552 | 52 | 0.90 |
| O(13) | 246 | 544 | 17 | 0.70 |
| O(14) | 241 | 527 | 157 | 0.60 |
| O(15) | 228 | 510 | −78 | 0.40 |
| O(16) | 179 | 490 | −73 | 0.40 |
| O(22) | 247 | 250 | −75 | 0.30 |
| O(23) | 311 | 250 | 202 | 0.30 |
| O(24) | 185 | 250 | 20 | 0.20 |
| O(25) | 201 | 250 | 110 | 0.20 |
| Cl(31) | 417 | 250 | 625 | 0.20 |
| Cl(32) | 458 | 250 | 688 | 0.20 |
| Cl(33) | 354 | 250 | 708 | 0.10 |
| O(31) | 385 | 208 | 668 | 0.50 |
| O(32) | 375 | 211 | 563 | 0.50 |
| O(33) | 469 | 250 | 783 | 0.20 |
| O(34) | 510 | 250 | 594 | 0.20 |
| O(35) | 333 | 250 | 604 | 0.20 |
| O(36) | 521 | 250 | 646 | 0.15 |
| O(37) | 417 | 250 | 510 | 0.15 |
| O(38) | 271 | 250 | 646 | 0.10 |
| H(1) | 327 | 439 | 265 | |
| H(2) | 478 | 486 | 306 | |
| H(3) | 606 | 475 | 173 | |
| H(4) | 576 | 438 | −29 | |
| H(61) | 443 | 357 | −111 | |
| H(62) | 442 | 413 | −174 | |
| H(101) | −3 | 328 | 59 | |
| H(102) | 2 | 390 | 83 | |
| H(12) | −32 | 315 | 282 | |
| H(13) | 53 | 295 | 451 | |
| H(14) | 225 | 328 | 481 | |
| H(15) | 297 | 360 | 309 | |

For O $B = 10.0$ A$^2$ and for H $B = 6.0$ A$^2$.

TABLE II. Bond Lengths (A) and Angles (°). Estimated standard deviations are given in parentheses.

(a) *Pd compound*

| | n = 1 | n = 2 | | n = 1 | n = 2 |
|---|---|---|---|---|---|
| Pd(n)–N(n1) | 2.07(4) | 1.97(3) | Pd(n)–N(n4) | 1.96(4) | 2.10(4) |
| Pd(n)–N(n2) | 2.02(3) | 2.06(3) | Pd(n)–N(n3) | 2.04(3) | 2.06(5) |
| N(n1)–C(n1) | 1.36(5) | 1.26(6) | N(n4)–C(n15) | 1.41(5) | 1.33(8) |
| C(n1)–C(n2) | 1.41(5) | 1.32(6) | C(n15)–C(n14) | 1.49(7) | 1.29(7) |
| C(n2)–C(n3) | 1.29(5) | 1.53(6) | C(n14)–C(n13) | 1.53(6) | 1.28(5) |
| C(n3)–C(n4) | 1.58(5) | 1.16(5) | C(n13)–C(n12) | 1.18(7) | 1.56(7) |
| C(n4)–C(n5) | 1.35(5) | 1.44(5) | C(n12)–C(n11) | 1.42(6) | 1.33(6) |
| C(n5)–N(n1) | 1.39(5) | 1.38(5) | C(n11)–N(n4) | 1.43(5) | 1.24(5) |
| C(n5)–C(n6) | 1.54(5) | 1.59(6) | C(n11)–C(n10) | 1.59(6) | 1.46(6) |
| C(n6)–N(n2) | 1.49(4) | 1.53(5) | C(n10)–N(n3) | 1.32(5) | 1.58(6) |
| N(n2)–C(n7) | 1.50(5) | 1.43(7) | N(n3)–C(n9) | 1.38(6) | 1.43(7) |
| C(n7)–C(n8) | 1.38(9) | 1.58(7) | C(n9)–C(n8) | 1.56(9) | 1.36(7) |
| Cl(n1)–O(n11) | 1.37(4) | 1.52(7) | Cl(n2)–O(n22) | 1.34(6) | 1.34(5) |
| Cl(n1)–O(n12) | 1.33(5) | 1.42(5) | Cl(n2)–O(n23) | 1.33(5) | 1.50(4) |
| Cl(n1)–O(n13) | 1.43(5) | 1.48(5) | Cl(n3)–O(n31) | 1.37(4) | 1.44(6) |
| Cl(n1)–O(n14) | 1.44(3) | 1.38(4) | Cl(n3)–O(n32) | 1.40(4) | 1.58(5) |
| Cl(n2)–O(n21) | 1.47(3) | 1.47(3) | Cl(n3)–O(n33) | 1.57(7) | 1.49(10) |

| | n = 1 | n = 2 | | n = 1 | n = 2 |
|---|---|---|---|---|---|
| N(n1)–Pd(n)–N(n2) | 80(1) | 83(1) | N(n4)–Pd(n)–N(n3) | 82(1) | 81(2) |
| N(n1)–Pd(n)–N(n4) | 102(2) | 104(1) | N(n2)–Pd(n)–N(n3) | 95(1) | 92(2) |
| N(n1)–Pd(n)–N(n3) | 175(1) | 175(2) | N(n2)–Pd(n)–N(n4) | 175(1) | 172(1) |
| Pd(n)–N(n1)–C(n1) | 128(3) | 132(3) | Pd(n)–N(n4)–C(n15) | 126(3) | 128(4) |
| Pd(n)–N(n1)–C(n5) | 114(3) | 113(3) | Pd(n)–N(n4)–C(n11) | 118(3) | 110(3) |
| C(n1)–N(n1)–C(n5) | 117(3) | 115(3) | C(n15)–N(n4)–C(n11) | 114(4) | 121(5) |
| C(n2)–C(n1)–N(n1) | 120(3) | 127(5) | C(n14)–C(n15)–N(n4) | 129(4) | 119(5) |
| C(n3)–C(n2)–C(n1) | 118(4) | 122(4) | C(n13)–C(n14)–C(n15) | 104(4) | 126(5) |
| C(n4)–C(n3)–C(n2) | 129(3) | 103(4) | C(n12)–C(n13)–C(n14) | 130(6) | 115(5) |
| C(n5)–C(n4)–C(n3) | 104(3) | 138(5) | C(n11)–C(n12)–C(n13) | 122(5) | 111(4) |
| N(n1)–C(n5)–C(n4) | 132(4) | 114(4) | N(n4)–C(n11)–C(n12) | 120(4) | 126(4) |
| N(n1)–C(n5)–C(n6) | 114(3) | 112(3) | N(n4)–C(n11)–C(n10) | 106(3) | 126(4) |
| C(n4)–C(n5)–C(n6) | 114(4) | 134(4) | C(n12)–C(n11)–C(n10) | 132(4) | 106(4) |
| C(n5)–C(n6)–N(n2) | 109(3) | 105(3) | C(n11)–C(n10)–N(n3) | 118(4) | 103(4) |
| Pd(n)–N(n2)–C(n6) | 111(2) | 99(2) | Pd(n)–N(n3)–C(n10) | 111(3) | 109(3) |
| Pd(n)–N(n2)–C(n7) | 114(2) | 108(3) | Pd(n)–N(n3)–C(n9) | 116(3) | 112(4) |
| C(n6)–N(n2)–C(n7) | 119(3) | 98(3) | C(n10)–N(n3)–C(n9) | 111(4) | 123(4) |
| N(n2)–C(n7)–C(n8) | 124(5) | 106(4) | N(n3)–C(n9)–C(n8) | 110(5) | 130(5) |
| C(n7)–C(n8)–C(n9) | 123(7) | 111(5) | | | |
| O(n11)–Cl(n1)–O(n12) | 108(3) | 114(3) | O(n21)–Cl(n2)–O(n21′)* | 113(2) | 100(2) |
| O(n11)–Cl(n1)–O(n13) | 117(3) | 104(3) | O(n21)–Cl(n2)–O(n22) | 109(2) | 113(2) |
| O(n11)–Cl(n1)–O(n14) | 117(3) | 105(3) | O(n21)–Cl(n2)–O(n23) | 111(2) | 109(2) |
| O(n12)–Cl(n1)–O(n13) | 100(3) | 103(3) | O(n22)–Cl(n2)–O(n23) | 104(3) | 113(3) |
| O(n12)–Cl(n1)–O(n14) | 102(2) | 121(3) | O(n31)–Cl(n3)–O(n31′)* | 108(3) | 119(5) |
| O(n13)–Cl(n1)–O(n14) | 110(3) | 109(3) | O(n31)–Cl(n3)–O(n32) | 108(2) | 90(4) |
| O(n32)–Cl(n3)–O(n33) | 105(3) | 92(5) | O(n31)–Cl(n3)–O(n33) | 115(3) | 120(3) |

*Atoms marked with a prime are related to those at *x*, *y*, *z* by –*x*, *y*, *z*.

(b) *Cu compound*

| | | | |
|---|---|---|---|
| Cu–N(1) | 2.01(2) | Cu–N(4) | 2.01(2) |
| Cu–N(2) | 2.01(3) | Cu–N(3) | 2.03(3) |
| Cu–O(11) | 2.64(3) | Cu–O(21) | 2.70(3) |
| N(1)–C(1) | 1.36(3) | N(4)–C(15) | 1.34(3) |
| C(1)–C(2) | 1.42(4) | C(15)–C(14) | 1.37(4) |
| C(2)–C(3) | 1.34(4) | C(14)–C(13) | 1.33(4) |

*(continued overleaf)*

TABLE II. *(continued)*

| | | | |
|---|---|---|---|
| C(3)–C(4) | 1.45(4) | C(13)–C(12) | 1.30(4) |
| C(4)–C(5) | 1.38(3) | C(12)–C(11) | 1.43(4) |
| C(5)–N(1) | 1.35(3) | C(11)–N(4) | 1.37(3) |
| C(5)–C(6) | 1.55(4) | C(11)–C(10) | 1.46(4) |
| C(6)–N(2) | 1.42(4) | C(10)–N(3) | 1.43(4) |
| N(2)–C(7) | 1.34(5) | N(3)–C(9) | 1.34(5) |
| C(7)–C(8) | 1.45(5) | C(9)–C(8) | 1.44(5) |
| Cl(1)–O(11) | 1.29(3) | Cl(2)–O(21) | 1.38(3) |
| | | | |
| N(1)–Cu–N(2) | 83(1) | N(4)–Cu–N(3) | 84(1) |
| N(1)–Cu–N(4) | 103(1) | N(2)–Cu–N(3) | 93(1) |
| N(1)–Cu–N(3) | 169(1) | N(4)–Cu–N(2) | 164(1) |
| N(1)–Cu–O(11) | 85(1) | N(4)–Cu–O(11) | 90(1) |
| N(1)–Cu–O(21) | 88(1) | N(4)–Cu–O(21) | 85(1) |
| N(2)–Cu–O(11) | 105(1) | N(3)–Cu–O(11) | 86(1) |
| N(2)–Cu–O(21) | 81(1) | N(3)–Cu–O(21) | 101(1) |
| O(11)–Cu–O(21) | 171(1) | | |
| Cu–O(11)–Cl(1) | 135(2) | Cu–O(21)–Cl(2) | 121(2) |
| Cu–N(1)–C(1) | 127(2) | Cu–N(4)–C(15) | 129(2) |
| Cu–N(1)–C(5) | 112(2) | Cu–N(4)–C(11) | 112(2) |
| Cu–N(2)–C(6) | 110(2) | Cu–N(3)–C(10) | 108(2) |
| Cu–N(2)–C(7) | 125(3) | Cu–N(3)–C(9) | 121(3) |
| C(1)–N(1)–C(5) | 121(2) | C(15)–N(4)–C(11) | 119(2) |
| N(1)–C(1)–C(2) | 121(3) | N(4)–C(15)–C(14) | 124(3) |
| C(1)–C(2)–C(3) | 119(3) | C(15)–C(14)–C(13) | 116(3) |
| C(2)–C(3)–C(4) | 119(3) | C(14)–C(13)–C(12) | 125(3) |
| C(3)–C(4)–C(5) | 119(3) | C(13)–C(12)–C(11) | 119(3) |
| C(4)–C(5)–N(1) | 121(3) | C(12)–C(11)–N(4) | 117(3) |
| C(4)–C(5)–C(6) | 123(3) | C(12)–C(11)–C(10) | 126(3) |
| N(1)–C(5)–C(6) | 116(2) | N(4)–C(11)–C(10) | 116(3) |
| C(5)–C(6)–N(2) | 110(3) | C(11)–C(10)–N(3) | 114(3) |
| C(6)–N(2)–C(7) | 120(4) | C(10)–N(3)–C(9) | 125(3) |
| N(2)–C(7)–C(8) | 120(4) | N(3)–C(9)–C(8) | 123(4) |
| C(7)–C(8)–C(9) | 127(4) | | |

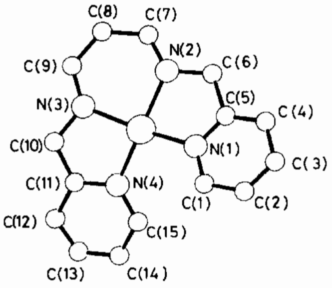


Fig. 1. The atom numbering system for the ligand.

(a) The two independent Pd cations and the perchlorate (1) anions in this lower symmetry structure are almost related by a *b*-glide perpendicular to *c*; the average deviation between such corresponding atoms is 0.21 Å and the range is 0.03 to 0.36 Å.

(b) However, the symmetry is more clearly broken by the other perchlorates (2) and (3); average deviation between corresponding atom positions is 1.07 Å with a much larger range 0.38 to 1.72 Å.

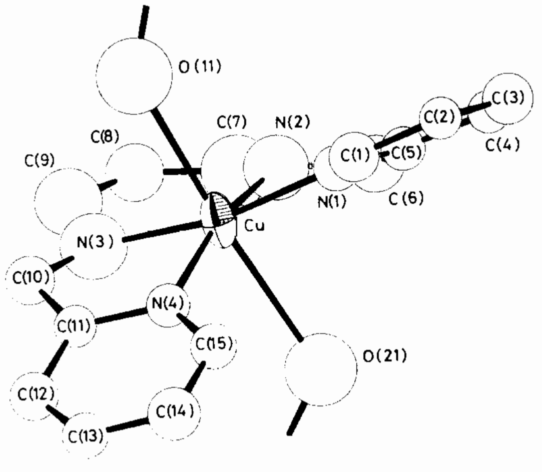


Fig. 2. Perspective drawing of the Cu cation including the perchlorate oxygen atoms. Thermal ellipsoids drawn to include 50% probability [6].

(c) Whereas, all independent perchlorate atom positions were clearly observed in the Pd compound,

TABLE III. Least-Squares Planes. Their equations are given by $lX + mY + nZ - p = 0$. Devaitions (A) of the most relevant atoms are given in square brackets.

| | *l* | *m* | *n* | *p* |
|---|---|---|---|---|
| (a) *Pd compounds* | | | | |
| Plane (1): Pd(1), N(11)–N(14) | 0.8822 | 0.4699 | 0.0299 | 3.3309 |
| [Pd(1) 0.01; N(11) 0.05; N(12) –0.06; N(13) 0.05; N(14) –0.05] | | | | |
| Plane (2): Pd(1), N(11), C(15), C(16), N(12) | 0.9421 | 0.3053 | –0.1386 | 3.5570 |
| [Pd(1) –0.16; N(11) 0.11; C(15) 0.01; C(16) –0.20; N(12) 0.24] | | | | |
| Plane (3): Pd(1), N(14), C(111), C(110), N(13) | 0.9378 | 0.3425 | 0.0570 | 3.4228 |
| [Pd(1) 0.09; N(14) –0.06; C(111) –0.02; C(110) 0.14; N(13) –0.15] | | | | |
| Plane (4): Pd(1), N(12), C(17)–C(19), N(13) | 0.9644 | 0.2641 | –0.0130 | 3.5270 |
| [Pd(1) 0.02; N(12) 0.23; C(17) –0.27; C(18) –0.04; C(19) 0.39; N(13) –0.33] | | | | |
| Plane (5): N(11), C(11)–C(15) | 0.8672 | 0.3534 | –0.3509 | 3.0236 |
| [N(11) –0.03; C(11) 0.02; C(12) 0.01; C(13) –0.01; C(14) $< \lvert 0.01 \rvert$; C(15) 0.02; C(16) 0.17] | | | | |
| Plane (6): N(14), C(111)–C(115) | 0.8847 | 0.3125 | 0.3458 | 3.8249 |
| [N(14) 0.02; C(111) 0.04; C(112) –0.05; C(113) 0.01; C(114) 0.05; C(115) –0.06; C(110) –0.26] | | | | |
| Plane (7): Pd(2), N(21)–N(24) | 0.8732 | 0.4728 | 0.1184 | 11.6206 |
| [Pd(2) –0.03; N(21) –0.02; N(22) 0.04; N(23) –0.03; N(24) 0.04] | | | | |
| Plane (8): Pd(2), N(21), C(25), C(26), N(22) | 0.9665 | 0.2247 | –0.1242 | 10.8018 |
| [Pd(2) 0.22; N(21) –0.13; C(25) –0.08; C(26) 0.35; N(22) –0.36] | | | | |
| Plane (9); Pd(2), N(24), C(211), C(210), N(23) | 0.9317 | 0.3282 | 0.1556 | 11.3901 |
| [Pd(2) –0.13; N(24) 0.04; C(211) 0.09; C(210) –0.22; N(23) 0.21] | | | | |
| Plane (10): Pd(2), N(22), C(27)–C(29), N(23) | 0.9591 | 0.2830 | 0.0029 | 11.2984 |
| [Pd(2) –0.04; N(22) –0.35; C(27) 0.54; C(28) –0.16; C(29) –0.26; N(23) 0.28] | | | | |
| Plane (11): N(21), C(21)–C(25) | 0.8926 | 0.3252 | –0.3124 | 11.0537 |
| [N(21) 0.02; C(21) 0.02; C(22) –0.04; C(23) 0.03; C(24) 0.01; C(25) –0.03; C(26) 0.05] | | | | |
| Plane (12): N(24), C(211)–C(215) | 0.8894 | 0.3053 | 0.3402 | 10.3486 |
| [N(24) –0.03; C(211) 0.07; C(212) –0.05; C(213) –0.01; C(214) 0.06; C(215) –0.04; C(210) $< \lvert 0.01 \rvert$] | | | | |
| (b) *Cu compound* | | | | |
| | *l* | *m* | *n* | *p* |
| Plane (1): Cu, N(1)–N(4) | –0.4074 | 0.9132 | 0.0117 | 7.8666 |
| [Cu 0.04; N(1) 0.20; N(2) –0.23; N(3) 0.21; N(4) –0.21] | | | | |
| Plane (2): N(1), C(1)–C(5) | –0.3276 | 0.8624 | –0.3860 | 7.4444 |
| [N(1) 0.02; C(1) –0.02; C(2) 0.02; C(3) –0.01; C(4) 0.01; C(5) –0.01; Cu –0.01; C(6) 0.03] | | | | |
| Plane (3): N(4), C(11)–C(15) | –0.2617 | 0.8991 | 0.3510 | 8.6952 |
| [N(4) –0.03; C(11) 0.01; C(12) 0.01; C(13) –0.02; C(14) <0.01; C(15) 0.02; Cu –0.26; C(10) –0.06] | | | | |
| Plane (4): Cu, N(1), C(5), C(6), N(2) | –0.2729 | 0.9247 | –0.2653 | 8.4550 |
| [Cu –0.14; N(1) 0.10; C(5) 0.01; C(6) –0.17; N(2) 0.21] | | | | |
| Plane (5): Cu, N(4), C(11), C(10), N(3) | –0.2449 | 0.9572 | 0.1545 | 8.8683 |
| [Cu 0.10; N(4) –0.06; C(11) –0.04; C(10) 0.15; N(3) –0.16] | | | | |
| Plane (6): Cu, N(2), C(7), C(8), C(9), N(3) | –0.1735 | 0.9837 | –0.0479 | 9.3010 |
| [Cu 0.06; N(2) 0.10; C(7) –0.18; C(8) 0.06; C(9) 0.15; N(3) –0.19] | | | | |

a distinct disordering of both position and occupancy of sites was found in the Cu analogue. Only the two perchlorato-oxygen atoms nearest the Cu were clearly defined. Such disorder allows the high symmetry space group, and there may be also some (averaged) disorder in the Cu cations.

The relationship between the two structures is shown in the packing diagrams of Fig. 3. These also show that the molecular cations are held in dimeric units, with the metal atoms bridged by one perchlorate. Two further perchlorates are associated with the metals, 'terminating' the dimers, and the fourth perchlorate is in general position not directly associated with the cations.

Within the molecular cations, bond lengths and angles show no unexpected features. The tetraamine ligand has the predicted [1] 'twist' conformation, defined by the need of the terminal pyridyl residues to twist away from one another to minimise steric interactions between the 6- and 6'-H atoms. As predicted [1], the $[CuN_4]$ polyhedron shows a much more distinct tetrahedral twist in response to steric constraints of the tetraamine than does the $[PdN_4]$ polyhedron (see Table III).

TABLE IV. The Geometries of Perchlorate Interactions with the N–H Groups.

| Angles (°) at N | N···O | Distances (Å) | Angles (°) of O···N subtended at N |
|---|---|---|---|
| C(6)<br>110<br>Cu—N(2) 120<br>125<br>C(7) | O(16) | 3.22 | Cu 72; C(6) 119; C(7) 100 |
| C(9)<br>121<br>Cu–N(3) 125<br>108<br>C(10) | O(22) | 3.13 | Cu 86; C(9) 112; C(10) 93 |
| | O(34$^{I}$) | 3.33 | Cu 136; C(9) 79; C(10) 83 |
| C(16)<br>114<br>Pd(1)–N(12) 120<br>111<br>C(17) | O(211$^{II}$) | 3.03 | Pd(1) 106; C(16) 90; C(17) 77 |
| | O(212) | 3.28 | Pd(1) 130; C(16) 85; C(17) 93 |
| C(19)<br>116<br>Pd(1)–N(13) 111<br>111<br>C(110) | O(223) | 3.07 | Pd(1) 88; C(19) 131; C(110) 97 |
| | O(132) | 3.16 | Pd(1) 143; C(19) 90; C(110) 81 |
| C(26)<br>100<br>Pd(2)—N(22) 98<br>108<br>C(27) | O(111$^{III}$) | 3.04 | Pd(2) 95; C(26) 100; C(27) 91 |
| | O(112) | 3.34 | Pd(2) 86; C(26) 105; C(27) 151 |
| C(29)<br>113<br>Pd(2)—N(23) 123<br>109<br>C(210) | O(223$^{II}$) | 3.30 | Pd(2) 136; C(29) 80; C(210) 96 |
| | O(123$^{IV}$) | 3.35 | Pd(2) 89; C(29) 105; C(210) 113 |

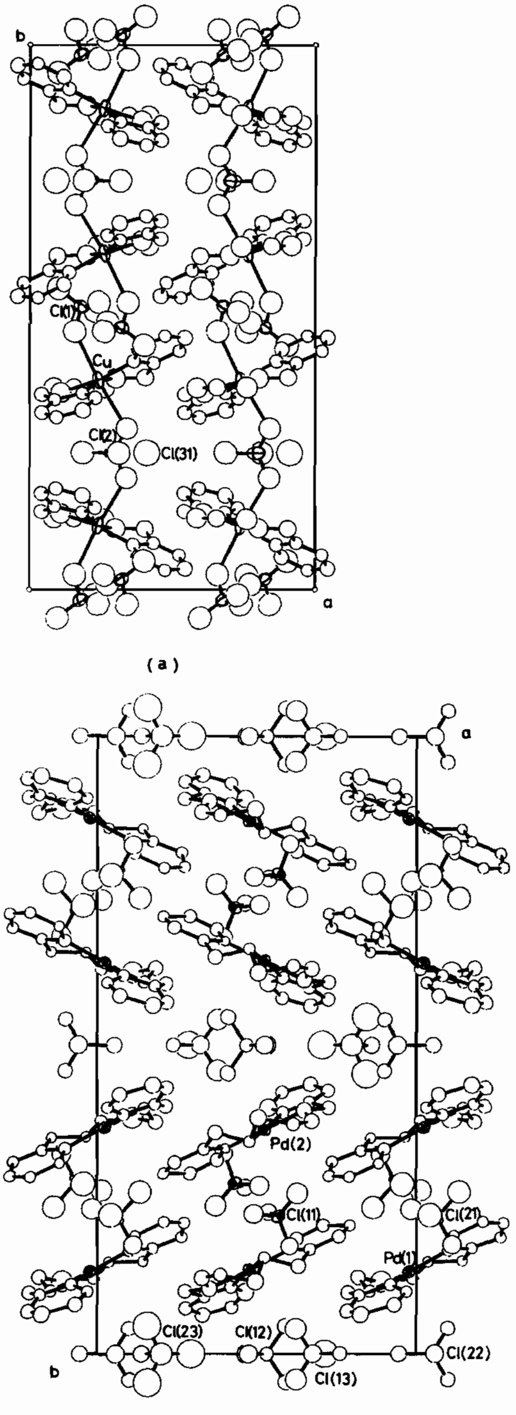
Roman numerical superscripts define atom positions relative to $x, y, z$:

I, $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$
II, $\frac{1}{2} - x, \bar{y}, z - \frac{1}{2}$
III, $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$
IV, $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$

A major contrast between the two structures is in the degree of bonding between the metals and the perchlorates. The Cu–O(1) and Cu–O(2) distances of 2.64(3) and 2.70(3) Å, respectively, are a clear indication of bonding. These distances are experimentally identical with that found in a more accurate determination of a closely-related compound 1,8-bis-(2′-pyridyl)-3,6-diazaoctane-copper(II) perchlorate [5]. By contrast the Pd···O distances (Pd(1)···O(213) 3.23, Pd(1)···O(221) 3.04, Pd(2)···O(113) 3.18, Pd(2)···O(121) {at $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$} 2.93 Å) are distinctly longer and the Pd···O directions also deviate more from perpendicularity with the [$MN_4$] planes than do the Cu–O directions: the range for the Pd compound being 6–17° to be compared with 6–7° for the Cu analogue.

Some intermolecular contacts for carbon atom (of cation) to oxygen atom (of anion) down to 3.0 Å were observed. However, their significance is uncertain in view of the high thermal parameters or the disorder in the perchlorate ions.

Figure 4 shows part of the i.r. spectra of the two compounds. They are reproducible on different instruments at different times. The pair of bands at 3620 and 3540 cm$^{-1}$ are typical of ‘free’ water molecules. Recrystallization of the copper compound from $D_2O$ [Fig. 4(c)] does not affect these bands [1], and now our structural determinations show that there are no water molecules in the crystalline structure. Hence, either, these bands do not result from O–H stretching frequencies at all [1], or, they indicate a surface phenomenon: water mole-



(a)

(b)

Fig. 3. Packing diagrams for both structures. (a) The Cu compound; for the 'free' perchlorate, only the position of Cl(31) is included for clarity. (b) The Pd compound.

cules adsorbed from the atmosphere at discrete independent surface sites, and not hydrogen bonded one to another. We now prefer the latter explanation.

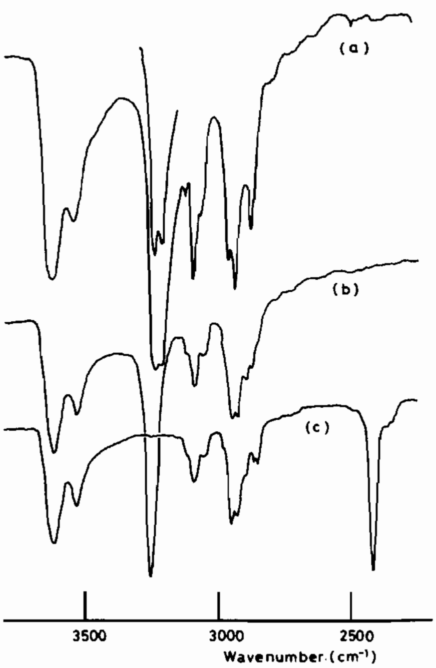


Fig. 4. The i.r. spectra of (a) the Pd compound; (b) the Cu compound; and (c) the Cu compound recrystallised from $D_2O$.

The N–H frequencies near 3300 cm$^{-1}$ are consistent with weak H-bonding shown by the relatively long O···(H) N distances observed (none <3.03 Å – Table IV). However, the presence of some weak H-bonding (or at least polarisation effects) offers the best explanation of the two N–H bands in the Pd compound (Fig. 4). Whereas the O···N distances in the Cu compound are not experimentally distinguished (Table IV) and are relatively long, there are two different classes of N···O interactions in the Pd compound. Three of the palladium N–H groups have perchlorate oxygens near 3.05 Å – appropriately placed to affect the N–H vibrations (and equally so) – whereas the fourth N–H group has no oxygens closer than 3.30 Å to the nitrogen. This difference of more than 0.2 Å at this level, seems a perfectly adequate reason for the two $\nu_{N-H}$ bands. An alternate argument, based on site symmetry, hardly seems tenable in these closely related structures.

Table IV gives some of the evidence for disorder in the Cu cations. The sums of angles at each nitrogen are 355.6°, whereas the corresponding values for the Pd structure are much closer to that expected for ideal tetrahedral geometry.

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