

the structure is that O(5) completes a distorted octahedron about the Cu atom. The Cu...O(5) distance of 4.011 (9) Å is, however, too long to represent a chemical bond.

References

Gmelins Handbuch der Anorganischen Chemie (1952). *Kupfer*, Syst. No. 60. Teil B, Lief 1, p. 572. Weinheim: Verlag Chemie.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1971). *ORTEPII*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

MOROSIN, B. (1969). *Acta Cryst.* **B25**, 19–30.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

VARGHESE, J. N. & MASLEN, E. N. (1985). *Acta Cryst.* **B41**, 184–190.

Acta Cryst. (1989). **C45**, 887–890

Structures of 1,8-Naphthyridine Silver(I) Perchlorate, Quinoxaline Silver(I) Perchlorate and Phthalazine Silver(I) Nitrate

BY TSUMIYOSHI TSUDA, SHIGERU OHBA, MACHIKO TAKAHASHI AND MASATOKI ITO

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223, Japan

(Received 6 October 1988; accepted 7 December 1988)

Abstract. Bis(μ -1,8-naphthyridine- N,N')-disilver(I)-($Ag-Ag$) diperchlorate, $[Ag_2(C_8H_6N_2)_2] \cdot 2ClO_4$, (I), $M_r = 675.0$, monoclinic, $P2_1/a$, $a = 16.114$ (3), $b = 10.462$ (2), $c = 5.772$ (1) Å, $\beta = 100.77$ (2)°, $V = 956.0$ (3) Å³, $Z = 2$, $D_x = 2.36$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 2.38$ mm⁻¹, $F(000) = 164$, $T = 298$ (1) K, $R = 0.026$ for 1586 unique reflections. catena-Poly[silver(I)- μ -quinoxaline- N,N'] perchlorate, $[Ag(C_8H_6N_2)] \cdot ClO_4$, (II), $M_r = 337.5$, orthorhombic, $Pmc2_1$, $a = 7.211$ (2), $b = 6.992$ (2), $c = 20.375$ (5) Å, $V = 1027.3$ (4) Å³, $Z = 4$, $D_x = 2.18$ Mg m⁻³, $\mu = 2.28$ mm⁻¹, $F(000) = 164$, $T = 297$ (1) K, $R = 0.023$ for 1223 unique reflections. Bis(μ -phthalazine- N,N')-bis(phthalazine- N)disilver(I) dinitrate, $[Ag_2(C_8H_6N_2)_4] \cdot 2NO_3$, (III), $M_r = 860.4$, monoclinic, $P2_1/a$, $a = 13.603$ (2), $b = 15.961$ (2), $c = 7.328$ (1) Å, $\beta = 99.10$ (2)°, $V = 1571.1$ (5) Å³, $Z = 2$, $D_x = 1.83$ Mg m⁻³, $\mu = 1.30$ mm⁻¹, $F(000) = 214$, $T = 298$ (1) K, $R = 0.034$ for 1526 unique reflections. In (I), a planar binuclear silver complex is formed with two 1,8-naphthyridine molecules as bridged ligands. In (II), Ag⁺ cations and quinoxaline molecules are arranged alternately to form one-dimensional chains along a . In (III), each Ag atom is surrounded trigonally by the N atoms of one unidentate and two bridging phthalazine molecules to form a nearly planar binuclear silver complex. The binuclear silver complexes in (I) and (III) have a center of symmetry, the Ag–Ag distances being (I) 2.756 (1) and (III) 3.491 (1) Å.

Introduction. Although a number of techniques concerning surface analysis have been developed, it is quite

difficult to elucidate the exact structure of adsorbate molecules on a metal surface. There is still controversy whether surface complexes formed by adsorption of molecules on a metal surface can be represented by metal complexes with the molecules as ligands (Rhodin & Ertl, 1979). Based on the many available data, there are good grounds for expecting metal complexes to be surface-structure models though no direct evidence for surface structure has been reported so far. We have recently reported the surface enhanced Raman scattering (SERS) results of azanaphthalene compounds on an Ag electrode surface (Takahashi, Furukawa, Fujita & Ito, 1987; Takahashi, Sakai, Fujita & Ito, 1986) and discussed the structure and orientation of the adsorbed molecules in relation to SER spectra. On the other hand, no structure data for azanaphthalene–silver complexes were available. In this study, we have determined the structures of the title complexes to investigate the correlation with the spectroscopic results.

Experimental. Colorless crystals were obtained by mixing AgClO₄ (or AgNO₃) and the diazanaphthalene in acetone. Rigaku AFC-5 diffractometer, graphite monochromator. Unit-cell parameters from 20–24 reflections ($20 < 2\theta < 31^\circ$). $2\theta_{max} = 55^\circ$, five standard reflections. After absorption correction, the structure was solved based on Patterson function or by direct methods with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms located in difference synthesis and refined isotropically. $\sum w(|F_o| - |F_c|)^2$ minimized, $w^{-1} =$

Table 1. Atomic positional parameters ($\times 10^4$, for Ag $\times 10^5$) and equivalent isotropic temperature factors (Hamilton, 1959)

| (I) | x | y | z | B _{eq} (Å ² × 10) |
|-------|-----------|-----------|-----------|---------------------------------------|
| Ag | 2973 (2) | 12097 (3) | 46773 (5) | 31 |
| Cl | 1621 (1) | 3847 (1) | 5721 (2) | 26 |
| O(1) | 848 (2) | 3570 (3) | 4079 (5) | 41 |
| O(2) | 1463 (2) | 3748 (3) | 8074 (5) | 40 |
| O(3) | 2250 (2) | 2932 (3) | 5372 (5) | 40 |
| O(4) | 1901 (2) | 5104 (3) | 5286 (6) | 45 |
| N(1) | -916 (2) | -287 (3) | 7941 (5) | 22 |
| C(2) | -1321 (2) | -1062 (3) | 9156 (6) | 27 |
| C(3) | -1737 (2) | -650 (4) | 10955 (6) | 30 |
| C(4) | -1724 (2) | 601 (4) | 11518 (6) | 30 |
| C(5) | -1274 (2) | 2801 (4) | 10713 (6) | 31 |
| C(6) | -887 (2) | 3581 (4) | 9392 (7) | 34 |
| C(7) | -515 (2) | 3042 (3) | 7623 (7) | 28 |
| N(8) | -501 (2) | 1800 (3) | 7169 (5) | 23 |
| C(9) | -909 (2) | 999 (3) | 8452 (5) | 21 |
| C(10) | -1308 (2) | 1476 (3) | 10269 (6) | 24 |

| (II) | x | y | z | B _{eq} (Å ² × 10) |
|--------|----------|------------|-----------|---------------------------------------|
| Ag(1) | 0 | 9010 (8) | 67281 (3) | 33 |
| Ag(2) | 0 | 50730 (10) | 94796 (4) | 35 |
| Cl(1) | 0 | 443 (2) | 8577 (1) | 33 |
| Cl(2) | 0 | 5757 (2) | 6351 (1) | 36 |
| O(1-1) | 0 | -915 (9) | 9095 (3) | 43 |
| O(2-1) | 0 | -485 (10) | 7956 (3) | 49 |
| O(3-1) | 1616 (8) | 1598 (9) | 8632 (3) | 85 |
| O(1-2) | 0 | 4806 (10) | 6981 (3) | 50 |
| O(2-2) | 0 | 4342 (9) | 5837 (3) | 48 |
| O(3-2) | 1624 (8) | 6870 (9) | 6315 (3) | 91 |
| N(1-1) | 3061 (4) | 1072 (5) | 6694 (2) | 28 |
| C(2-1) | 4004 (6) | 1334 (7) | 7223 (2) | 33 |
| C(7-1) | 4034 (7) | 263 (8) | 4946 (3) | 37 |
| C(8-1) | 3069 (6) | 550 (7) | 5518 (3) | 33 |
| C(9-1) | 4034 (5) | 809 (6) | 6113 (2) | 25 |
| N(1-2) | 3051 (4) | 5081 (6) | 9476 (2) | 28 |
| C(2-2) | 4000 (6) | 4698 (7) | 10001 (2) | 30 |
| C(7-2) | 4035 (7) | 6381 (9) | 7771 (2) | 40 |
| C(8-2) | 3059 (6) | 5956 (8) | 8329 (3) | 33 |
| C(9-2) | 4024 (5) | 5500 (5) | 8911 (2) | 24 |

| (III) | x | y | z | B _{eq} (Å ² × 10) |
|---------|-----------|-----------|-----------|---------------------------------------|
| Ag | 93756 (4) | 8814 (3) | 39940 (7) | 42 |
| C(1-1) | 9384 (4) | -1754 (3) | 2440 (8) | 32 |
| N(2-1) | 9510 (3) | -1027 (3) | 3259 (6) | 31 |
| N(3-1) | 9265 (4) | -294 (3) | 2282 (6) | 32 |
| C(4-1) | 8929 (4) | -351 (3) | 480 (8) | 30 |
| C(5-1) | 8467 (4) | -1163 (4) | -2439 (8) | 34 |
| C(6-1) | 8332 (5) | -1933 (4) | -3227 (8) | 38 |
| C(7-1) | 8512 (4) | -2681 (4) | -2208 (8) | 36 |
| C(8-1) | 8852 (4) | -2637 (4) | -332 (8) | 32 |
| C(9-1) | 9006 (4) | -1852 (3) | 521 (7) | 27 |
| C(10-1) | 8804 (4) | -1115 (3) | -492 (7) | 28 |
| C(1-2) | 8787 (4) | 2360 (4) | 1049 (8) | 35 |
| N(2-2) | 9082 (4) | 2191 (3) | 2803 (7) | 35 |
| N(3-2) | 9349 (4) | 2836 (3) | 4023 (7) | 38 |
| C(4-2) | 9280 (5) | 3606 (4) | 3430 (8) | 38 |
| C(5-2) | 8865 (5) | 4672 (4) | 916 (9) | 42 |
| C(6-2) | 8542 (5) | 4819 (4) | -917 (10) | 48 |
| C(7-2) | 8309 (5) | 4153 (4) | -2195 (9) | 46 |
| C(8-2) | 8383 (5) | 3351 (4) | -1608 (8) | 42 |
| C(9-2) | 8706 (4) | 3180 (3) | 298 (8) | 29 |
| C(10-2) | 8956 (4) | 3833 (3) | 1555 (8) | 31 |
| N | 7456 (4) | 1048 (3) | 6276 (7) | 45 |
| O(1) | 7497 (6) | 645 (3) | 4935 (8) | 94 |
| O(2) | 8208 (6) | 1129 (4) | 7326 (11) | 119 |
| O(3) | 6720 (6) | 1367 (5) | 6561 (12) | 131 |

Table 2. Bond lengths (Å) and bond angles (°)

| (I) | Bond length (Å) | Bond angle (°) | |
|--------------------|-----------------|----------------|-----------|
| Ag-Ag ⁱ | 2.756 (1) | C(2)-C(3) | 1.405 (5) |
| Ag-N(8) | 2.190 (3) | C(3)-C(4) | 1.348 (6) |
| Ag-N(1) | 2.185 (3) | C(4)-C(10) | 1.410 (5) |
| Cl-O(1) | 1.447 (3) | C(5)-C(6) | 1.347 (6) |
| Cl-O(2) | 1.432 (3) | C(5)-C(10) | 1.409 (5) |
| Cl-O(3) | 1.435 (4) | C(6)-C(7) | 1.396 (6) |
| Cl-O(4) | 1.428 (3) | C(7)-N(8) | 1.327 (4) |
| N(1)-C(2) | 1.321 (5) | N(8)-C(9) | 1.366 (5) |
| N(1)-C(9) | 1.377 (4) | C(9)-C(10) | 1.419 (5) |

Table 2 (cont.)

| | | | |
|----------------------------|-----------|-----------------|-----------|
| Ag ⁱ -Ag-N(8) | 84.8 (1) | C(3)-C(4)-C(10) | 119.6 (3) |
| Ag-Ag ⁱ -N(1) | 84.4 (1) | C(6)-C(5)-C(10) | 120.0 (3) |
| O(1)-Cl-O(2) | 108.8 (2) | C(5)-C(6)-C(7) | 118.5 (4) |
| O(1)-Cl-O(3) | 108.6 (2) | C(6)-C(7)-N(8) | 124.4 (4) |
| O(1)-Cl-O(4) | 109.3 (2) | Ag-N(8)-C(7) | 116.1 (2) |
| O(2)-Cl-O(3) | 109.9 (2) | Ag-N(8)-C(9) | 125.8 (2) |
| O(2)-Cl-O(4) | 110.6 (2) | C(7)-N(8)-C(9) | 117.8 (3) |
| O(3)-Cl-O(4) | 109.6 (2) | N(1)-C(9)-N(8) | 118.0 (3) |
| Ag ⁱ -N(1)-C(2) | 115.5 (2) | N(1)-C(9)-C(10) | 121.0 (3) |
| Ag ⁱ -N(1)-C(9) | 126.4 (2) | N(8)-C(9)-C(10) | 121.0 (3) |
| C(2)-N(1)-C(9) | 118.1 (3) | C(4)-C(10)-C(5) | 123.5 (3) |
| N(1)-C(2)-C(3) | 123.7 (3) | C(4)-C(10)-C(9) | 118.3 (3) |
| C(2)-C(3)-C(4) | 119.2 (4) | C(5)-C(10)-C(9) | 118.2 (3) |

Symmetry code: (i) -x, -y, 1-z.

| (II) | Bond length (Å) | Bond angle (°) | |
|-----------------------|-----------------|-----------------------|------------|
| Ag(1)-N(1-1) | 2.212 (3) | C(7-1)-C(7-1') | 1.393 (10) |
| Ag(2)-N(1-2) | 2.200 (3) | C(7-1)-C(8-1) | 1.372 (8) |
| Cl(1)-O(1-1) | 1.420 (6) | C(8-1)-C(9-1) | 1.410 (7) |
| Cl(1)-O(2-1) | 1.422 (7) | C(9-1)-C(9-1') | 1.393 (7) |
| Cl(1)-O(3-1) | 1.422 (6) | N(1-2)-C(2-2) | 1.298 (6) |
| Cl(2)-O(1-2) | 1.446 (7) | N(1-2)-C(9-2) | 1.380 (5) |
| Cl(2)-O(2-2) | 1.441 (6) | C(2-2)-C(2-2') | 1.442 (9) |
| Cl(2)-O(3-2) | 1.408 (6) | C(7-2)-C(7-2') | 1.392 (10) |
| N(1-1)-C(2-1) | 1.288 (6) | C(7-2)-C(8-2) | 1.370 (7) |
| N(1-1)-C(9-1) | 1.388 (5) | C(8-2)-C(9-2) | 1.411 (7) |
| C(2-1)-C(2-1') | 1.436 (9) | C(9-2)-C(9-2') | 1.408 (7) |
| O(1-1)-Cl(1)-O(2-1) | 110.9 (4) | C(7-1)-C(8-1)-C(9-1) | 119.9 (4) |
| O(1-1)-Cl(1)-O(3-1) | 108.7 (4) | N(1-1)-C(9-1)-C(8-1) | 120.1 (4) |
| O(2-1)-Cl(1)-O(3-1) | 109.2 (4) | N(1-1)-C(9-1)-C(9-1') | 120.4 (4) |
| O(3-1)-Cl(1)-O(3-1') | 110.0 (4) | C(8-1)-C(9-1)-C(9-1') | 119.6 (4) |
| O(1-2)-Cl(2)-O(2-2) | 109.2 (4) | Ag(2)-N(1-2)-C(2-2) | 121.6 (3) |
| O(1-2)-Cl(2)-O(3-2) | 107.5 (4) | Ag(2)-N(1-2)-C(9-2) | 120.8 (3) |
| O(2-2)-Cl(2)-O(3-2) | 110.0 (4) | C(2-2)-N(1-2)-C(9-2) | 117.6 (3) |
| O(3-2)-Cl(2)-O(3-2') | 112.6 (4) | N(1-2)-C(2-2)-C(2-2') | 121.8 (4) |
| Ag(1)-N(1-1)-C(2-1) | 120.6 (3) | C(7-2)-C(7-2)-C(8-2) | 120.9 (5) |
| Ag(1)-N(1-1)-C(9-1) | 121.6 (3) | C(7-2)-C(8-2)-C(9-2) | 119.5 (4) |
| C(2-1)-N(1-1)-C(9-1) | 117.8 (3) | N(1-2)-C(9-2)-C(8-2) | 119.9 (4) |
| N(1-1)-C(2-1)-C(2-1') | 121.9 (4) | N(1-2)-C(9-2)-C(9-2') | 120.6 (4) |
| C(7-1)-C(7-1)-C(8-1) | 120.5 (5) | C(8-2)-C(9-2)-C(9-2') | 119.5 (4) |

Symmetry code: (i) 1-x, y, z; (ii) -x, y, z.

| (III) | Bond length (Å) | Bond angle (°) | |
|-------------------------|-----------------|--------------------------------|------------|
| Ag-N(3-1) | 2.249 (5) | C(1-2)-C(9-2) | 1.417 (8) |
| Ag-N(2-2) | 2.276 (5) | N(2-2)-N(3-2) | 1.374 (7) |
| C(1-1)-N(2-1) | 1.305 (7) | N(3-2)-C(4-2) | 1.302 (8) |
| C(1-1)-C(9-1) | 1.427 (7) | C(4-2)-C(10-2) | 1.422 (8) |
| N(2-1)-N(3-1) | 1.385 (7) | C(5-2)-C(6-2) | 1.366 (9) |
| N(3-1)-C(4-1) | 1.330 (7) | C(5-2)-C(10-2) | 1.418 (8) |
| C(4-1)-C(10-1) | 1.409 (7) | C(6-2)-C(7-2) | 1.419 (9) |
| C(5-1)-C(6-1) | 1.358 (9) | C(7-2)-C(8-2) | 1.349 (9) |
| C(5-1)-C(10-1) | 1.430 (8) | C(8-2)-C(9-2) | 1.423 (8) |
| C(6-1)-C(7-1) | 1.409 (9) | C(9-2)-C(10-2) | 1.397 (7) |
| C(7-1)-C(8-1) | 1.381 (8) | N-O(1) | 1.183 (8) |
| C(8-1)-C(9-1) | 1.401 (8) | N-O(2) | 1.186 (9) |
| C(9-1)-C(10-1) | 1.395 (7) | N-O(3) | 1.171 (10) |
| C(1-2)-N(2-2) | 1.313 (8) | | |
| N(3-1)-Ag-N(2-2) | 124.1 (2) | Ag-N(2-2)-C(1-2) | 124.9 (4) |
| N(2-1)-C(1-1)-C(9-1) | 123.4 (5) | Ag-N(2-2)-N(3-2) | 115.2 (3) |
| C(1-1)-N(2-1)-N(3-1) | 120.7 (4) | C(1-2)-N(2-2)-N(3-2) | 119.4 (5) |
| Ag-N(3-1)-N(2-1) | 115.3 (3) | N(2-2)-N(3-2)-C(4-2) | 119.5 (5) |
| Ag-N(3-1)-C(4-1) | 126.4 (4) | N(3-2)-C(4-2)-C(10-2) | 123.9 (5) |
| N(2-1)-N(3-1)-C(4-1) | 118.2 (5) | C(6-2)-C(5-2)-C(10-2) | 119.0 (6) |
| N(3-1)-C(4-1)-C(10-1) | 123.8 (5) | C(5-2)-C(6-2)-C(7-2) | 121.6 (6) |
| C(6-1)-C(5-1)-C(10-1) | 118.2 (5) | C(6-2)-C(7-2)-C(8-2) | 120.2 (6) |
| C(5-1)-C(6-1)-C(7-1) | 122.8 (6) | C(7-2)-C(8-2)-C(9-2) | 119.4 (6) |
| C(6-1)-C(7-1)-C(8-1) | 119.2 (6) | C(1-2)-C(9-2)-C(8-2) | 123.5 (5) |
| C(7-1)-C(8-1)-C(9-1) | 119.5 (5) | C(1-2)-C(9-2)-C(10-2) | 115.9 (5) |
| C(1-1)-C(9-1)-C(8-1) | 122.9 (5) | C(8-2)-C(9-2)-C(10-2) | 120.6 (5) |
| C(1-1)-C(9-1)-C(10-1) | 116.2 (4) | C(4-2)-C(10-2)-C(5-2) | 123.9 (5) |
| C(8-1)-C(9-1)-C(10-1) | 120.9 (5) | C(4-2)-C(10-2)-C(9-2) | 116.9 (5) |
| C(4-1)-C(10-1)-C(5-1) | 123.0 (5) | C(5-2)-C(10-2)-C(9-2) | 119.2 (5) |
| C(4-1)-C(10-1)-C(9-1) | 117.6 (4) | O(1)-N-O(2) | 116.7 (6) |
| C(5-1)-C(10-1)-C(9-1) | 119.4 (5) | O(1)-N-O(3) | 122.6 (7) |
| N(2-2)-C(1-2)-C(9-2) | 124.3 (5) | O(2)-N-O(3) | 120.7 (7) |
| Ag ⁱ -N(2-1) | 2.332 (4) | Ag ⁱ -N(2-1)-C(1-1) | 120.4 (3) |
| H(1-2)...H(4-1) | 2.61 (7) | Ag ⁱ -N(2-1)-N(3-1) | 115.6 (3) |
| N(3-2)...H(1-1') | 2.35 (5) | N(2-1)-Ag-N(2-2) | 106.9 (2) |
| | | N(3-1)-Ag-N(2-1') | 122.8 (2) |
| | | N(3-2)...H(1-1')-C(1-1') | 148.9 (4) |

Symmetry code: (i) 2-x, -y, 1-z.

$\sigma^2(|F_o|) + (0.015|F_c|)^2$. Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974), computation program system UNICSIII (Sakurai & Kobayashi, 1979).^{*} Final atomic parameters are listed in Table 1, and bond lengths and angles in Table 2. Experimental details are as follows. (I): Crystal size 0.10 × 0.24 × 0.40 mm, monoclinic, $-20 \leq h \leq 20$, $0 \leq k \leq 13$, $0 \leq l \leq 7$, θ - 2θ scan, 2406 reflections measured, 1742 observed reflections $[|F_o| > 3\sigma(|F_o|)]$, 1586 unique ($R_{int} = 0.010$). Space group $P2_1/a$ from systematic absences, $0.61 < A < 0.80$, final $R = 0.026$, $wR = 0.029$, $S = 1.17$, $\Delta/\sigma < 0.22$ for non-H atoms, $-0.59 < \Delta\rho < 0.64 \text{ e } \text{Å}^{-3}$. (II): Crystal size 0.35 × 0.30 × 0.60 mm, orthorhombic, $-9 \leq h \leq 9$, $0 \leq k \leq 26$, $-9 \leq l \leq 9$, ω scan, 4650 reflections measured, 4178 observed reflections, 1223 unique ($R_{int} = 0.016$), $0.47 < A < 0.55$. Systematic absences $hk0$, k odd indicated three possible space groups, $\bar{a}cb$ setting of $Pmc2_1$ (No. 26), cab setting of $Pma2$ (No. 28), or $b\bar{a}c$ setting of $Pmma$ (No. 51). Space group was determined as $Pmc2_1$ by the successful solution after changing the indices hkl to $\bar{h}\bar{k}l$. No mirror symmetry perpendicular to c in the derived structure excluded the possibility of other two space groups. The absolute structure could not be determined. Final $R = 0.023$, $wR = 0.030$, $S = 1.58$, $\Delta/\sigma < 0.24$ for non-H atoms, $-0.71 < \Delta\rho < 0.61 \text{ e } \text{Å}^{-3}$. (III): Crystal size 0.10 × 0.10 × 0.70 mm, monoclinic, $-17 \leq h \leq 17$, $0 \leq k \leq 20$, $0 \leq l \leq 9$, θ - 2θ scan, 3883 reflections measured, 1649 observed reflections, 1526 unique ($R_{int} = 0.013$). Space group $P2_1/a$, $0.80 < A < 0.91$, final $R = 0.034$, $wR = 0.037$, $S = 1.41$, $\Delta/\sigma < 0.26$ for non-H atoms, $-0.38 < \Delta\rho < 0.59 \text{ e } \text{Å}^{-3}$.

Discussion. ORTEP (Johnson, 1965) drawings of the complex cations are presented in Fig. 1. The bond lengths and angles of the counter ions, ClO_4 or NO_3 , and the contacts between complex cations and these anions in (I) to (III) are omitted from the text because the values are quite normal. (I) and (III) are planar binuclear complexes having a center of symmetry. The deviation of the Ag atoms from the diazanaphthalene planes is less than 0.3 Å. The Ag—Ag distances are (I) 2.756 (1) Å, which is slightly shorter than the nearest-neighbor distance in silver metal, 2.88 Å, and (III) 3.491 (1) Å. The quinoxaline compound (II) forms a linear polymer along a , where two independent Ag⁺ ions lie on a mirror perpendicular to a . The structure is very similar to that of pyrazinesilver(I) nitrate (Vranka & Amma, 1966). The average Ag—N bond distances

are (I) 2.188 (3), (II) 2.206 (3) and (III) 2.286 (5) Å. The slightly longer Ag—N distance in (III) is due to the coordination number of the Ag⁺ ion which is larger than in (I) and (II). The N(2-1')—Ag—N(2-2) angle of (III) is smaller by 17.2 (2)° than the N(3-1)—Ag—N(2-2) angle because of H(1-2)···H(4-1) repulsion and N(3-2)···H(1-1') attraction. The Ag—N—C (or N)

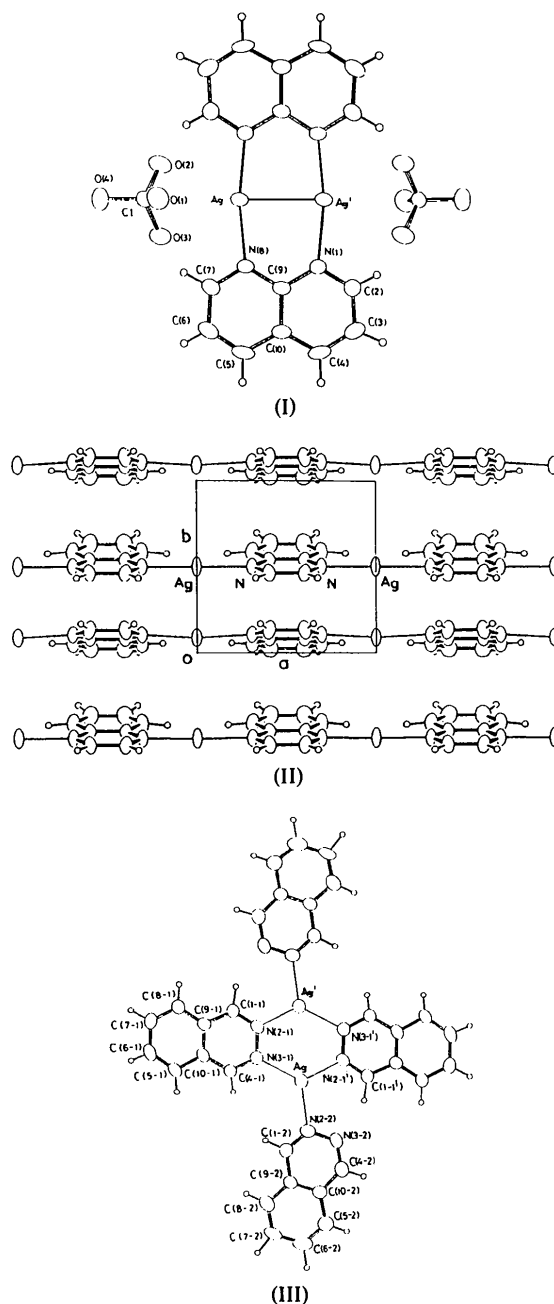


Fig. 1. ORTEP plots of the complex molecule in (I) and complex cations in (III) with labeling scheme and partial projection of the crystal structure of (II) along c . The counter anions, ClO_4^- in (II) and NO_3^- in (III), are omitted from the figure. The symmetry code is given in Table 2.

^{*} Lists of structure factors, anisotropic thermal parameters, atomic parameters for H atoms and bond lengths and bond angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51677 (53 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bond angles are (I) 115.5 (2)–126.4 (2), (II) 120.6 (3)–121.6 (3), and (III) 115.3 (3)–126.4 (4)°, suggesting that the lone-pair lobes of the N atoms are directed approximately towards the Ag⁺ ions. In (I) and (II), the complex cations exhibit simple and straightforward coordination geometries through the two N atoms of the diazanaphthalene molecules, and are consistent with SER spectra. The structure of (III) is also in harmony with the expectation from the SERS study that phthalazine displays two kinds of adsorptions, unidentate and bridged, on a silver surface, depending upon the electrode potentials.

References

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

Acta Cryst. (1989). **C45**, 890–892

Structure of a Pentacoordinate Complex of Bis(diphenyldithiophosphinato)cobalt(II) with 3-Methylpyridine

BY KALYAN DAS, U. C. SINHA* AND R. N. MUKHERJEE

Department of Physics and Department of Chemistry, Indian Institute of Technology, Bombay-400076, India

AND RAKESH BOHRA

Department of Chemistry, University of Rajasthan, Jaipur-302016, India

(Received 11 October 1988; accepted 7 December 1988)

Abstract. Bis(diphenyldithiophosphinato)(3-methylpyridine)cobalt(II), [Co(C₆H₇N){P(C₆H₅)₂S₂}]₂, *M_r* = 650.69, orthorhombic, *Fdd*2, *a* = 23.964 (4), *b* = 28.274 (7), *c* = 9.209 (5) Å, *V* = 6240.42 Å³, *Z* = 8, *D_m* = 1.33 (by flotation in aqueous Zn solution), *D_x* = 1.385 Mg m⁻³, λ(Mo Kα) = 0.71069 Å, μ = 0.87 mm⁻¹, *F*(000) = 2664.00, *T* = 295 K, final *R* = 0.029 for 1179 reflections. The coordination polyhedron around the Co^{II} ion is a distorted trigonal bipyramid. The S atoms in the bidentate diphenyldithiophosphinato (dtpi) ligand are coordinated to the metal in both axial and equatorial directions.

Introduction. Dithio acid ions such as dtpi are able to form four-membered chelates with 3*d* transition metals. The Co atom has an almost tetrahedral coordination environment in [Co(dtpi)₂], so the introduction of another ligand severely affects the coordination geometry. The pentacoordinated complexes [Co(dtpi)₂-

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

RHODIN, T. N. & ERTL, G. (1979). *The Nature of the Surface Chemical Bond*. Oxford: North-Holland.

SAKURAI, T. & KOBAYASHI, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77.

TAKAHASHI, M., FURUKAWA, H., FUJITA, M. & ITO, M. (1987). *J. Phys. Chem.* **91**, 5940–5943.

TAKAHASHI, M., SAKAI, Y., FUJITA, M. & ITO, M. (1986). *Surf. Sci.* **176**, 351–366.

VRANKA, R. G. & AMMA, E. L. (1966). *Inorg. Chem.* **5**, 1020–1025.

(*L*)], where *L* represents 2-, 3- and 4-methylpyridine, 2-aminopyridine, quinoline and isoquinoline, are found to be quite stable in the solid state. The 1:1 adduct with a monodentate axial ligand like 2-, 3- or 4-methylpyridine can have a trigonal bipyramidal or a square pyramidal configuration. In order to find the exact coordination geometry around the Co^{II} ion, X-ray diffraction studies of the 3-methylpyridine derivative were carried out. The 2-methylpyridine adduct is isomorphous to the 3-methylpyridine adduct (Patel & Sinha, 1977) but owing to steric effects the latter is found to be more stable.

Experimental. The heterocyclic amine was added in excess to a solution of cobalt chloride hexahydrate in methanol. To this blue solution the calculated amount of sulfur ligand (dtpiH) was added and the required complex separated almost immediately. It was crystallized from a chloroform–methanol mixture (Mukherjee, Venkateshan & Zingde, 1974).

Blue crystal of dimensions 0.2 × 0.2 × 0.2 mm; Enraf–Nonius CAD-4 diffractometer, graphite-mono-

*To whom correspondence should be addressed at Department of Physics.