Acknowledgment. We thank the National Science Foundation (Grant No. CHE 86-19420) and the Robert A. Welch Foundation (Grant No. A-648) for financial support and M. F. Guest for providing the GAMESS package of programs. This research was conducted in part with use of the Cornell National Supercomputer Facility, a resource for the Center for Theory and Simulation in Science and Engineering at Cornell University, which is funded in part by the National Science Foundation, New York State, and the IBM Corp.

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Dinuclear Pt(II), Pd(II), Ni(II), and Cu(II) Complexes of 3,5-Pyrazoledicarboxylic Acid

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There is much current interest in dinuclear metal complexes from the standpoint of catalysis,[1] biological mimicry,[2] multielectron-transfer reactions,[3] and metal–metal interactions.[4] Among ligands capable of forming dinuclear complexes, there has been a very strong interest in pyrazoles.[5-10] This heterocycle has been extensively employed in pyrazolylborates,[11] to stabilize a variety of organometallic and coordination compounds. In much of the recent work, interest has focused on the ability of the pyrazole ring to hold two metals ions in close proximity and on controlling the properties of the metal ion by the substitution at the 3- and 5-positions.

We have become particularly interested in the 3,5-dicarboxypyrazoles, which are easily synthesized.[12] These planar, heteroaromatic dicarboxylates have a number of attractive features. They are sterically compact, allow metal–metal interactions through π orbitals, and can carry substantial negative charge. In view of these features they have been investigated surprisingly little although there have been significant studies on *pyrazine*-dicarboxylates, which have yielded a number of interesting compounds.[13] In the five-membered diaza ring system we have shown that the imidazoledicarboxylates can form trianionic planar chelates with two metal ions under appropriate conditions.[14] However, the pyrazoledicarboxylates hold the metal ions even closer. Here we report synthetic and structural results on complexes of 3,5-pyazoledicarboxylic acid (H_3Dcp) as a dinucleating, trianionic ligand.

Complexes of this ligand, with metals that can sustain square-planar coordination, can result in planar dinuclear anions. Not only can such ions potentially stack and undergo partial oxidation but they can be precipitated with cations that are themselves capable of forming anisotropic conductors or that are magnetically active. The resulting products should resemble the better known mononuclear systems, which lead to one-dimensional metals in the case of oxalates and cyanides[15] and magnetic chains in the case of copper complexes.[16] The feature of planar metal–metal interaction in addition to the stacking interaction may lead to interesting modifications of physical properties.[17]

Experimental Section

$(NBu_4)_2[Pt_2(Dcp)_2]$ was prepared by dissolving 3,5-dicarboxypyrazole monohydrate (Fluka) (160 mg, 0.92 mmol) in 20 mL of hot water. The solution was mixed with 0.46 mmol of H_2PtCl_4 in 10 mL of water. Addition of 1.78 mL of NBu_4OH (40% in water) (2.76 mmol) produces a mixture of white and red precipitates. Addition of 10 mL of acetonitrile dissolves the red precipitate, presumably $(NBu_4)_2PtCl_4$. Reduction of solvent volume by half followed by cooling leads to precipitation of a white solid. Recrystallization from acetonitrile–water yields 120 mg (45%) of analytically pure product. IR (KBr pellet): $\nu(COO)_{as}$ 1647 cm^{-1}. Anal. Calcd for $C_{42}N_6H_{74}O_8Pt_2$: C, 42.71; H, 6.31; N, 7.11. Found: C, 42.96; H, 6.23; N, 7.31.

Table I. Summary of Crystal Data for Complexes $(NBu_4)_2[M_2(Dcp)2]$ (M = Pd, Cu)

	$(NBu_4)_2[Pd_2(Dcp)_2]$	$(NBu_4)_2[Cu_2(Dcp)_2]$
space group	$P\bar{1}$	$P\bar{1}$
a, Å	11.290 (3)	10.899 (4)
b, Å	11.893 (4)	12.286 (5)
c, Å	10.775 (3)	9.899 (3)
α, deg	107.95 (3)	109.51 (3)
β, deg	100.05 (3)	101.88 (3)
γ, deg	113.26 (2)	102.69 (3)
V	1187.7 (7)	1161.3 (8)
Z	1	1
cryst dimens, mm	0.36 × 0.31 × 0.17	0.31 × 0.18 × 0.42
calcd density, g cm^{-3}	1.40	1.31
abs coeff, cm^{-1}	15.15	9.42
formula	$C_{42}H_{74}N_6O_8Pd_2$	$C_{42}H_{74}N_6O_8Cu_2$
fw	1003.9	918.2
radiation, Å	0.710 69	0.710 69
no. of unique rfls	4202	3066
no. of obs rfls ($F_o^2 \geq 3\sigma(F_o^2)$)	3583	2374
R	0.048	0.043
R_w	0.048	0.044

$(NBu_4)_2[Pd_2(Dcp)_2]$. A 100-mg sample of $PdCl_2$ (0.56 mmol) and 1.47 mg of 3,5-dicarboxypyrazole monohydrate (0.84 mmol) were stirred in 20 mL of hot water. When all the solids had dissolved, 1.27 mL (1.95 mmol) of NBu_4OH (40% in water) was added, producing a yellow precipitate. Recrystallization from acetonitrile–water yields shiny yellow

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Table II. Atomic Coordinates ($\times 10^4$) for $(NBu_4)_2[Pd_2(Dcp)_2]$

atom	*x*	*y*	*z*
Pd	0.0523 (0)	0.3610 (0)	0.4350 (0)
N1	−0.0826 (4)	0.3961 (4)	0.3425 (4)
N3	0.1176 (4)	0.5092 (4)	0.6130 (4)
O2	−0.0244 (4)	0.2090 (4)	0.2407 (4)
O1	−0.1670 (5)	0.1340 (4)	0.0268 (4)
O3	0.1980 (4)	0.3348 (4)	0.5481 (5)
O4	0.3529 (4)	0.4236 (5)	0.7587 (5)
C3	−0.1564 (5)	0.3162 (5)	0.2082 (5)
C1	−0.1170 (6)	0.2102 (5)	0.1500 (6)
C4	−0.2445 (6)	0.3609 (6)	0.1651 (6)
C8	0.2171 (5)	0.5270 (6)	0.7180 (6)
C6	0.2622 (6)	0.4225 (6)	0.6761 (7)
N5	1.2525 (4)	1.2455 (4)	1.0079 (4)
C11	0.2793 (5)	0.3898 (5)	1.0521 (5)
C15	0.1884 (6)	0.4255 (6)	1.1259 (6)
C19	0.2226 (7)	0.5704 (6)	1.1531 (7)
C23	0.1432 (9)	0.6209 (8)	1.2300 (9)
C12	0.2663 (5)	0.2074 (5)	1.1299 (5)
C16	0.4062 (6)	0.2914 (6)	1.2428 (6)
C20	0.4011 (6)	0.2559 (6)	1.3659 (7)
C24	0.5389 (8)	0.3347 (8)	1.4819 (8)
C13	0.3565 (5)	0.2386 (5)	0.9374 (6)
C17	0.3488 (6)	0.1018 (6)	0.8779 (6)
C21	0.4479 (7)	0.1064 (7)	0.7977 (7)
C25	0.4443 (10)	−0.0268 (10)	0.7341 (10)
C14	0.1060 (5)	0.1455 (5)	0.9087 (5)
C18	0.0646 (6)	0.1634 (6)	0.7768 (6)
C22	−0.0806 (7)	0.0510 (7)	0.6879 (7)
C26	−0.1310 (8)	0.0586 (8)	0.5533 (8)

needles (220 mg, 78%). IR (KBr pellet): $\nu(COO)_{as}$ 1642 cm^{-1}. Anal. Calcd for $C_{42}N_6H_{74}O_8Pd_2$: C, 50.25; H, 7.47; N, 8.37. Found: C, 50.60; H, 7.51; N, 8.37.

$(NBu_4)_2[Ni_2(Dcp)_2]$ was prepared by dissolving $Ni(NO_3)_2 \cdot 6H_2O$ (0.1678 g, 0.57 mmol) in 10 mL of DMSO and 20 mL of H_2O. This was mixed with a solution of dicarboxypyrazole monohydrate (0.100 g, 0.57 mmol) in 10 mL of DMSO, and a light blue precipitate formed. A 1-mL aliquot of NBu_4OH (40% in water) was added, and the volume of the solution was reduced to 7 mL by heating. A 40-mL volume of DMSO was added and the volume again reduced to approximately 10 mL by heating. Upon cooling, orange crystals formed, which were filtered out, washed with 2-propanol, and dried under vacuum at 100 °C. Yield: 0.144 g, 44%. IR (KBr pellet): $\nu(COO)_{as}$ 1649 cm^{-1}. Anal. Calcd for $C_{42}H_{74}N_6O_8Ni_2$: C, 55.53; H, 8.21; N, 9.25. Found: C, 55.54; H, 7.79; N, 9.34. Crystal data: a = 10.953 Å, b = 12.253 Å, c = 9.924 Å, α = 109.29°, β = 102.49°, γ = 103.24°, V = 1160.2 Å^3.

$(NBu_4)_2[Cu_2(Dcp)_2]$. To a suspension of 174 mg of 3,5-dicarboxypyrazole monohydrate (1 mmol) in 100 mL of hot acetonitrile was added 242 mg of $Cu(NO_3)_2 \cdot 3H_2O$ with stirring. Addition of 33 mL of 0.1 M NBu_4OH in toluene–methanol (3.3 mmol) caused the solids to dissolve and a dark blue solution to form. After 10 min of reflux, the hot solution was filtered and the solvents were allowed to evaporate to a volume of several milliliters. The dark blue solid was filtered out and washed with 20 mL of ether. The yield was nearly quantitative. IR (KBr pellet): $\nu(COO)_{as}$ 1608 cm^{-1}. Anal. Calcd for $C_{42}N_6H_{74}O_8Cu_2$: C, 54.94; H, 8.12; N, 9.15. Found: C, 55.29; H, 8.30; N, 9.09.

Physical Measurements. IR spectra were recorded as KBr pellets with a Perkin-Elmer 1710 spectrometer. Electrochemical oxidations were performed at either constant current or constant voltage with a Sambrook Engineering (Wales, U.K.) power supply. The magnetic data were gathered on a Quantum Design Model MPMS instrument, and the data workup followed standard methods.[18] X-ray diffraction data were gathered on a Syntex $P2_1$ diffractometer. The structures of both copper and palladium complex salts of the tetrabutylammonium ion were solved in the space group $P\bar{1}$. The structure solutions were routine with conditions and procedures having been previously described.[19] A test of refinement in the alternate space group $P1$ was not judged to be a significant improvement over $P\bar{1}$ considering the increased number of parameters. Although the two structures have slightly different cell parameters, they are nearly isomorphous. The parameters used during the X-ray data collection are summarized in Table I.

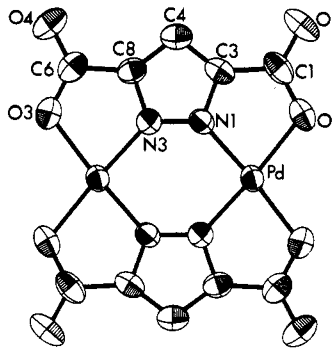

Figure 1. ORTEP view of the complex anion.

Table III. Atomic Coordinates ($\times 10^4$) for $(NBu_4)_2[Cu_2(Dcp)_2]$

atom	*x*	*y*	*z*
Cu	0.3158 (1)	0.9422 (1)	0.3650 (1)
N1	0.4110 (4)	0.8808 (4)	0.4908 (5)
N3	0.4661 (4)	1.0791 (4)	0.4158 (5)
O2	0.1737 (3)	0.7965 (3)	0.3257 (4)
O1	0.1266 (4)	0.6420 (3)	0.3993 (4)
O3	0.2365 (3)	1.0156 (3)	0.2362 (4)
O4	0.2946 (4)	1.1603 (4)	0.1475 (4)
C3	0.3444 (5)	0.7806 (4)	0.5018 (5)
C1	0.2030 (5)	0.7324 (5)	0.4019 (6)
C4	0.5738 (5)	1.2451 (4)	0.3936 (6)
C8	0.4546 (5)	1.1526 (4)	0.3443 (5)
C6	0.3192 (6)	1.1080 (5)	0.2341 (6)
N5	0.0318 (4)	0.7455 (3)	−0.1998 (4)
C11	0.0547 (4)	0.8774 (4)	−0.1819 (5)
C12	0.1151 (5)	0.9134 (4)	−0.2913 (6)
C13	0.1250 (5)	1.0453 (5)	−0.2612 (6)
C14	0.1803 (6)	1.0880 (5)	−0.3703 (6)
C21	−0.0544 (5)	0.6563 (4)	−0.3585 (5)
C22	−0.1878 (5)	0.6700 (4)	−0.4140 (5)
C23	−0.2523 (6)	0.5816 (5)	−0.5773 (6)
C24	−0.3908 (6)	0.5789 (6)	−0.6408 (7)
C31	−0.0340 (5)	0.7334 (4)	−0.0807 (5)
C32	−0.0567 (6)	0.6135 (5)	−0.0637 (7)
C33	−0.1452 (6)	0.6065 (5)	0.0357 (7)
C34	−0.2840 (7)	0.5859 (7)	−0.0357 (9)
C41	0.1592 (5)	0.7129 (5)	−0.1792 (6)
C42	0.2641 (6)	0.7876 (5)	−0.0306 (7)
C43	0.3826 (7)	0.7424 (8)	−0.0259 (8)
C44	0.4867 (8)	0.7994 (10)	0.1113 (10)

Table IV. Selected Bond Distances (Å) for Complexes $(NBu_4)_2[M_2(Dcp)_2]$ (M = Cu, Pd)

	M = Cu	M = Pd		M = Cu	M = Pd
M–N1	1.907 (04)	1.927 (04)	O1–C1	1.222 (05)	1.223 (07)
M–N3	1.911 (04)	1.930 (04)	O3–C6	1.295 (06)	1.297 (07)
M–O2	1.955 (03)	2.050 (04)	O4–O6	1.252 (06)	1.227 (07)
M–O3	1.960 (03)	2.056 (04)	C3–C1	1.511 (07)	1.494 (08)
N1–C3	1.336 (06)	1.341 (06)	C3–C4	1.389 (06)	1.378 (08)
N1–N3	1.338 (06)	1.318 (06)	C4–C8	1.392 (06)	1.401 (07)
N3–N8	1.331 (06)	1.344 (06)	C8–C6	1.500 (07)	1.498 (08)
O2–C1	1.304 (06)	1.309 (07)	M–M′	3.978 (01)	3.888 (01)

Table V. Selected Angles (deg) for Complexes $(NBu_4)_2[M_2(Dcp)_2]$ (M = Cu, Pd)

	M = Cu	M = Pd		M = Cu	M = Pd
N1–M–N3	92.4 (2)	96.6 (2)	N3–M–O3	81.7 (2)	78.9 (2)
N1–M–O2	81.7 (2)	79.6 (2)	O2–M–O3	104.1 (1)	104.9 (2)

Results and Discussion

To simplify the discussion, we will refer to the palladium structure unless otherwise stated. A view of the structure of the complex anion is shown in Figure 1. The same labeling has been

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[19] Computations were carried out on an Amdahl 5860 computer. Computer programs used during the structural analysis were from the SHELX program package by George Sheldrick, Institut fur Anorganische Chemie der Universitat Gottingen, FRG. Other program include ORTEP, by C. K. Johnson, PLUTO, a crystallographic plotting program, and GEOMIN, a geometry calculation program supplied by University Chemical Laboratory, Cambridge, England.

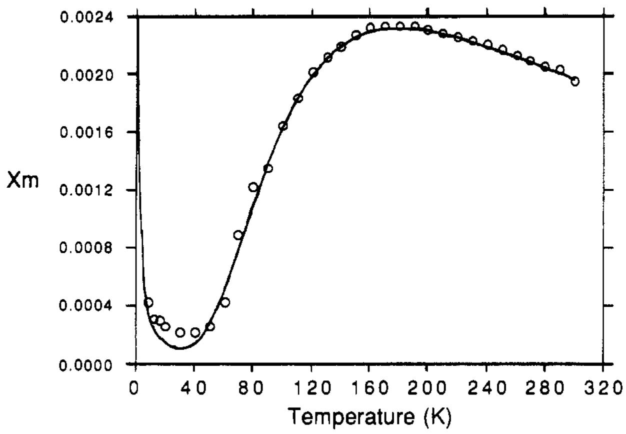

Figure 2. Plot of χ_m vs temperature.

used for the copper complex. The atomic coordinates are given in Tables II and III. The dinuclear complex is centrosymmetric and most of the bond lengths and angles (Tables IV and V) are compatible with D_{2h} symmetry within experimental error. In fact all atoms of the anion lie within 0.1 Å of the best mean plane, an indication of low strain throughout the complex. The cell parameters for the nickel complex are very similar to those of the palladium and copper complexes although in this case no intensity data were gathered. The tetrabutylammonium ion prevents close intermolecular stacking of the planar anions. We have reported on the effects of cation size on anion stacking elsewhere,[20] and further investigation is underway in this system. It is noteworthy, however, that the tetrabutylammonium ion adopts a relatively flat shape to accommodate to the shape of the rigid planar anion. The four terminal carbon atoms of the butyl groups are nearly coplanar, thus alleviating, in part, the problem of packing "basketballs and pizza pans". The bite angle of O–Pd–N is approximately the same as that found in the 4,5-dicarboxyimidazole complex with rhodium,[14] again indicating that a favorable geometry is available with this ligand.

An intriguing feature of the structure is the relatively short metal–metal separation of 3.89 Å (3.99 Å for Cu–Cu) resulting from the formation of a six-membered bimetallacyclic ring. This distance is very similar to the distance observed in a structurally related (aminotriazole)copper complex recently reported.[22] The copper ion's proximity leads to a significant coupling both through-space and through the π system of the heteroaromatic pyrazole rings. To test this factor, we investigated the magnetic behavior as a function of temperature. Figure 2 shows the data and the theoretical fitting to a modified Bleaney–Bowers relationship.[18] With use of a small correction for paramagnetic impurity ($q = 0.004$ (1), $c = 0.375$) and a value for g of 2.09 (14), an antiferromagnetic coupling constant of $2J = -200.2$ (8) cm^{-1} can be calculated. This value is lower than those observed for dinuclear copper complexes unsymmetrically bridged by a single pyrazole and a simple monoatomic bridge, but in those cases the Cu–Cu distances are nearly an 1 Å shorter.[23] Presumably this substantial interaction results from strong participation by the heteroaromatic pyrazole orbitals in the metal–nitrogen metallacyclic ring.

Attempts to partially oxidize the platinum complex were made by placing an acetonitrile solution into the anode compartment of an electrochemical cell with NBu_4Br as the supporting electrolyte. The current values were very low up to the oxidation potential of bromine, and no solid formed on the electrode. Subsequent attempts to carry out full oxidation with bromine gave products that analyzed for oxidative addition of two bromine atoms to each metal ion as well as addition of bromine to the 4-position of the pyrazole rings. Such reactions of pyrazole have been observed previously with chlorine.[24] Attempts at electrochemical oxidation of the sodium and potassium salts of the platinum complex, in the absence of supporting electrolyte, gave no reaction although these conditions yield "cation deficient" oxidation products with oxalates and cyanides.

The conditions necessary to form partially oxidized anisotropically conducting solids require delicate control of counterions and ligand electronic character. Although the dicarboxypyrazolate complexes are electronically and sterically very similar to the oxalate complexes that form conducting solids, it has not so far been possible to mimic those properties in our dinuclear systems. For example, the sodium, potassium, and alkaline-earth salts of our platinum complex are too insoluble to allow their use in electrochemical oxidations. In addition, it may be necessary to modify the electronic character of the ligand in order to observe the eclipsed stacking we have achieved in the imidazole systems.[14] These ligand modifications through substitution at the 4-position will be a part of our future work. In a very recent paper,[25] the authors stated that doubly bridging pyrazole–copper complexes were not known. We are pleased to be able to change the situation by this report. It is perhaps because of the additional charge compensation offered by the dicarboxy derivatives that these complexes form so readily. The availability of planar, dinuclear, anionic complexes opens many possibilities for studies of magnetism, catalysis, and intermolecular interactions.

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Supplementary Material Available: Tables of thermal parameters (1 page); tables of structure factors (13 pages). Ordering information is given on any current masthead page.

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Halogenoargentates(I) with Unusual Coordination Geometries. Synthesis and Structure of Potassium–Crypt Salts of Chloro-, Bromo-, and Iodoargentates(I), Including the First Example of a Two-Coordinated Chloroargentate(I) in the Solid State[1]

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The coordination number most commonly exhibited by silver(I) in crystalline halogenoargentates(I) is undoubtedly 4.[2] Thus, the majority of such compounds whose structures have been deter-

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(1) Work presented in part at the International Union of Crystallography XV Congress and General Assembly, Bordeaux, France, 1990, and at International Conference on Coordination Chemistry XXVIII, Gera, Germany, 1990.
(2) Jagner, S.; Helgesson, G. *Adv. Inorg. Chem.*, in press.