Howard-Lock, H. E., LeBlanc, D. J., Lock, C. J. L., Smith, R. W. & Wang, Z. (1996). *J. Chem. Soc. Chem. Commun.* pp. 1391–1392.
Isab, A. A. & Sadler, P. J. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1657–1663.
Schmidbaur, H., Dziwok, A., Grohmann, A. & Müller, G. (1989). *Chem. Ber.* **122**, 893–895.
Schmidbaur, H., Graf, W. & Müller, G. (1988). *Angew. Chem. Int. Ed. Engl.* **27**, 419–421.
Schröter, I. & Strähle, J. (1991). *Chem. Ber.* **124**, 2161–2164.
Sheldrick, G. M. (1994). *SHELXTL. Structure Determination Programs.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1996). *SADABS. Program for Applying Absorption and Decay Corrections to Area Detector Data.* University of Göttingen, Germany.
Siemens (1996*a*). *SAINT.* Version 4.05. *Program for Reduction of Raw Area Detector Data.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996*b*). *SMART.* Version 4.05. *Package for Data Collection and Integration.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (1994). *Am. Crystallogr. Assoc. Meet.* Abstracts, paper M05.
Spek, A. L. (1997). *PLATON. Molecular Geometry Program.* Version of March 1997. University of Utrecht, The Netherlands.
Wojnowski, W., Becker, B., Sabmannshausen, J., Peters, E. M., Peters, K. & von Schnering, H. G. (1994). *Z. Anorg. Allg. Chem.* **620**, 1417–1421.

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A New Perylene Salt: Diperylenium(1+) Bis[quinoxaline-2,3-dithiolato(2–)-*S*,*S*′]-cuprate(III)

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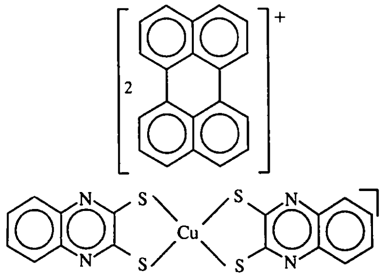
Abstract

A new perylene salt, $(C_{20}H_{12})_2[Cu(C_8H_4N_2S_2)_2]$, $(per)_2[Cu(qdt)_2]$, has been prepared by electrocrystallization and characterized by single-crystal X-ray diffraction. The crystal structure consists of tetramerized stacks of perylene species along the *c* axis, with three crystallographically independent interplanar distances, 3.50 (1), 3.42 (1) and 3.55 (1) Å. These tetramers are flanked by a centrosymmetrically related pair of $[Cu(qdt)_2]^-$ anions.

Comment

Perylene is an electron-donor molecule which has been widely used in the preparation of several molecular compounds exhibiting high electrical conductivity and even metallic properties. Different acceptor counterions have been employed to produce these materials, from I_3^- to several metal–dithiolate complexes (Almeida & Henriques, 1997). Our group has investigated extensively the $(per)[M(mnt)_2]$ (mnt is maleonitriledithiolate or *cis*-2,3-dimercapto-2-butenedinitrile) family of molecular conductors (Gama *et al.*, 1993). The specific redox properties of $[M(mnt)_2]$ anions make them particularly good acceptor counterions and the possible use of different metals allows manipulation of the physical properties of those materials. As part of an effort to obtain new molecular conductors based on perylene, we modified the $(per)_2[M(mnt)_2]$ materials by substitution of the acceptor anion with other planar metallic complexes.

Complexes of quinoxaline-2,3-dithiolate (qdt) are analogous to metal–bis(dithiolenes) and include pyrazine rings which can also undergo redox reactions and provide advantageous interactions with an electron donor. They therefore appear to be good candidates for combination with perylene.



$(per)_2[Cu(qdt)_2]$

The crystal structure of $(per)_2[Cu(qdt)_2]$ (Fig. 1) consist of tetramerized stacks of perylene units along the *c* axis, separated by centrosymmetrically-related pairs of $[Cu(qdt)_2]^-$ anions (Fig. 2). The unit cell contains two independent perylene species [per(*A*) and per(*B*)] and one independent $[Cu(qdt)_2]^-$ anion, which are at general positions. The two perylene units are planar and have, within experimental uncertainty, the same bond distances and angles. The charge of the $[Cu(qdt)_2]^-$ anion can be assigned by comparison of the Cu—S bond distances (2.18 Å average) with those in $(PPh_4)_2[Cu^{II}(qdt)_2]$ and $(PPh_4)_2[Cu^{III}(qdt)_2]$ (Boyde, Garner & Clegg, 1987). Consequently, the charge balance indicates one positive charge for every two $C_{20}H_{12}$ units in the stacks. The perylene stacks, consisting of the repeat $B—A—A^i—B^i$ [symmetry code: (i) $1-x$, $1-y$, $1-z$], are well separated in the *ab* plane by anions and no interstack contacts exist in the **a** direction. The two perylene units are planar and almost parallel [their normal makes an angle of 2.44 (6)°] and

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the dihedral angles to the [Cu(qdt)$_2$] species are per(*A*)–[Cu(qdt)$_2$] 74.29 (5)° and per(*B*)–[Cu(qdt)$_2$] 71.90 (5)°. The perylene species have a normal at *ca* 26° to the *c* axis [per(*A*) 25.94 (5) and per(*B*) 26.07 (5)°] and the [Cu(qdt)$_2$] species has a normal at 80.50 (5)° to the same axis. Within the stacks, the three crystallographically independent interplanar distances are *A*—*B* 3.50 (1), *B*—*B*$^{\text{i}}$ 3.42 (1) and *A*—*A*$^{\text{i}}$ 3.55 (1) Å. The [Cu(qdt)$_2$]$^-$ anion is essentially planar, the angle between the $\mathrm{CuS_4}$ and $\mathrm{C_8N_2S_2}$ planes is 1.51 (8)° {*cf.* 20° in $\mathrm{(PPh_4)_2[Cu^{III}(qdt)_2]}$} (Boyde, Garner & Clegg, 1987).

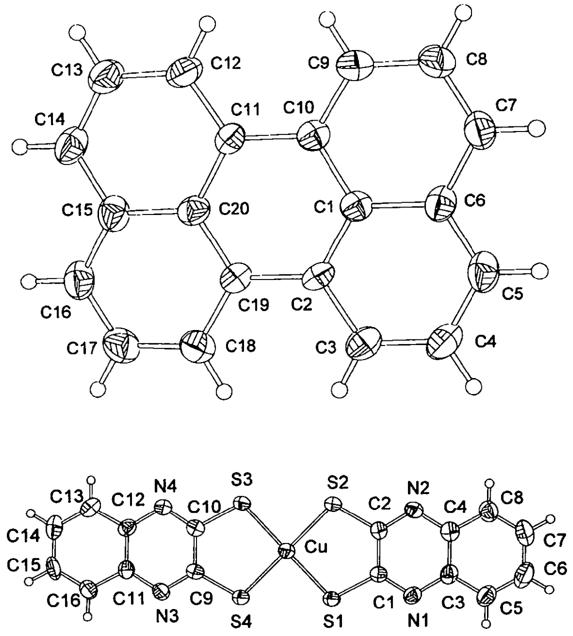

Fig. 1. Views of the '*A*' perylene molecule and the [Cu(qdt)$_2$]$^-$ anion with the atomic numbering scheme and displacement ellipsoids at the 40% probability level. The '*B*' perylene molecule is very similar. H atoms are shown as spheres of arbitrary radii.

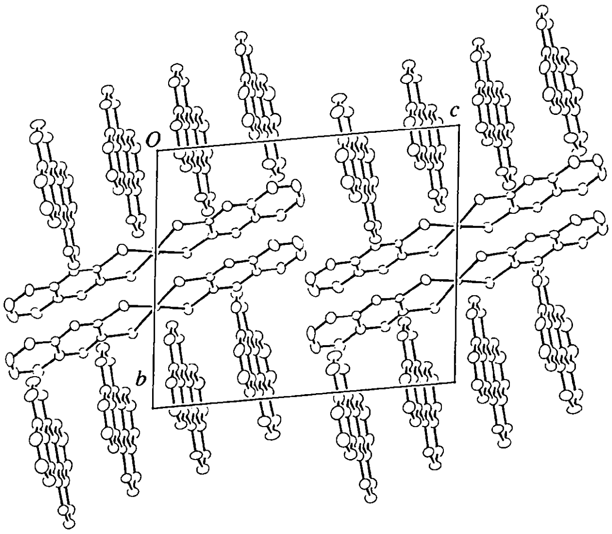

Fig 2. Projection of the crystal structure along the *a* axis.

Interactions between the anions and the perylene molecule exist, as denoted by several N···H and S···H contacts below or in the range of the sum of the van der Waals radii. Those contacts may favour the tetramerization of the perylene stacks, a quite different situation from the α-phase of the family of one-dimensional conductors (per)$_2$[*M*(mnt)$_2$], where the disposition of the acceptor counterions as segregated stacks favours the regular perylene stacks and consequently the metallic properties of the material (Domingos *et al.*, 1988).

Experimental

Single crystals of (per)$_2$[Cu(qdt)$_2$] were obtained on the anode of an electrochemical cell where oxidation of perylene is carried out in a dichloromethane-THF (1:1) solution (10^{-2} *M*) containing $\mathrm{(PPh_4)[Cu^{III}(qdt)_2]}$ (50 mg in 40 ml of solution). In turn, this reagent was prepared according to the procedure described in the literature (Theriot, Ganguli, Kavarnos & Bernal, 1969; Boyde, Garner & Clegg, 1987). Elemental analysis was in good agreement with the crystallographically-determined stoichiometry.

Crystal data

$\mathrm{(C_{20}H_{12})_2[Cu(C_8H_4N_2S_2)_2]}$
$M_r = 952.64$
Triclinic
$P\overline{1}$
$a = 11.1451\ (12)$ Å
$b = 12.5674\ (8)$ Å
$c = 15.5207\ (12)$ Å
$\alpha = 95.374\ (8)°$
$\beta = 105.384\ (8)°$
$\gamma = 92.095\ (9)°$
$V = 2082.5\ (3)$ Å^3
$Z = 2$
$D_x = 1.519$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10$–$15°$
$\mu = 0.773$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.14 × 0.10 × 0.05 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scan
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.969$, $T_{\max} = 1.000$
10 409 measured reflections
10 041 independent reflections

4012 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.050$
$\theta_{\max} = 27.97°$
$h = -14 \rightarrow 14$
$k = -16 \rightarrow 16$
$l = -20 \rightarrow 0$
4 standard reflections every 200 reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.147$

$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.625$ e Å^{-3}
$\Delta\rho_{\min} = -0.413$ e Å^{-3}

$S = 1.128$
10035 reflections
587 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0143P)^2 + 3.8414P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu—S4	2.175 (2)	Cu—S3	2.179 (2)
Cu—S2	2.178 (2)	Cu—S1	2.179 (2)
S4—Cu—S2	178.17 (9)	S3—Cu—S1	177.00 (9)
S4—Cu—S3	92.79 (7)	C1—S1—Cu	104.6 (2)
S2—Cu—S3	87.20 (7)	C2—S2—Cu	103.8 (2)
S4—Cu—S1	87.18 (7)	C10—S3—Cu	104.2 (2)
S2—Cu—S1	92.74 (7)	C9—S4—Cu	104.3 (2)

Table 2. *Contact distances (Å)*

S1···H3B^{i}	2.87	C9···H9B^{ii}	2.78
S4···H12B^{ii}	2.94	C16···H18A^{iv}	2.79
N1···H9A^{iii}	2.63		

Symmetry codes: (i) $x, 1+y, z$; (ii) $1-x, 1-y, -z$; (iii) $1-x, 1-y, 1-z$; (iv) $x, 1+y, z-1$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1309). Services for accessing these data are described at the back of the journal.

References

Almeida, M. & Henriques, R. T. (1997). In *Organic Conductive Molecules and Polymers*, Vol. 1, edited by H. S. Nalwa, ch. 12. New York: John Wiley & Sons.

Boyde, S., Garner, C. D. & Clegg, W. (1987). *J. Chem. Soc. Dalton Trans.* pp. 1083–1087.

Domingos, A., Henriques, R. T., Gama, V., Almeida, M., Lopes Vieira, A. & Alcácer, L. (1988). *Synth. Met.* **27**, B411–B416.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Gama, V., Henriques, R. T., Bonfait, G., Almeida, M., Ravy, S., Pouget, J. P. & Alcácer, L. (1993). *Mol. Cryst. Liq. Cryst.* **234**, 171–178.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Theriot, L. J., Ganguli, K. K., Kavarnos, S. & Bernal, I. (1969). *J. Inorg. Nucl. Chem.* pp. 3133–3140.

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A Nickel(II) Compound with a Tetradentate Diamine–Diimine Ligand, (2,4,6,9,11-Pentamethyl-5,8-diazadodeca-4,8-diene-2,11-diamine)nickel(II) Tetrachlorozincate

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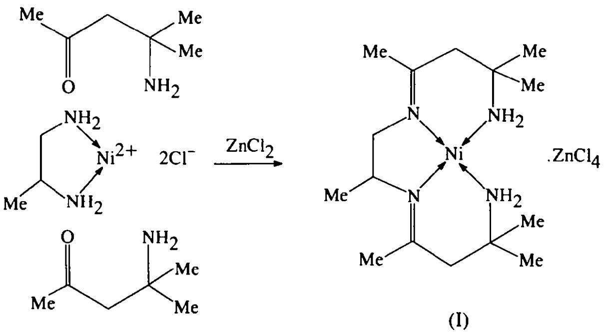
Abstract

The title compound, $[Ni(C_{15}H_{32}N_4)][ZnCl_4]$, has a tetradentate diamine–diimine ligand in a tetrahedrally twisted square-planar coordination to singlet ground-state nickel(II), with a mean Ni—N distance of 1.909 (3) Å. The cation has approximate mirror symmetry, apart from the axially oriented C6 methyl substituent.

Comment

Compounds with amine–imine ligands have been prepared by reaction of a variety of amine compounds of copper(II) and nickel(II) with 4-amino-4-methylpentan-2-one (Morgan & Curtis, 1980; Morgan, Martin & Curtis, 1979). The yellow diamagnetic title compound, [Ni(pnda)][$ZnCl_4$], (I), was prepared by reaction with tris(propane-1,2-diamine)nickel(II) tetrachlorozincate. The structures of (2,4-dimethyl-5,8-diazadec-4-ene-7,10-diamine)copper(II) tetrachlorozincate, formed from (3-azapentane-1,5-diamine)copper(II) (Gladkikh, Curtis & Heath, 1997), [Cu(pnda)]$(ClO_4)_2$ and the pentadentate ligand compound (2,4-dimethyl-5,8,11-triazatridec-4-ene-2,13-diamine)copper(II) perchlorate, formed by reaction with 3,6-diazaoctane-1,8-diamine)copper(II) perchlorate (Curtis, Gladkikh & Turnbull, 1997) have been described.



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