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Crystal structure of 6-ethylidene-4-vinyl-18,21-dioxa-15,24-dithia-2,5,8-triazatricyclo[23.4.0.0]nonacosa-1(25),4,9,11,13,26,28-heptaene-3,7-dione, $C_{25}H_{25}N_3O_4S_2$, *a 21-membered dioxa-dithia-diamide based macrocycle*

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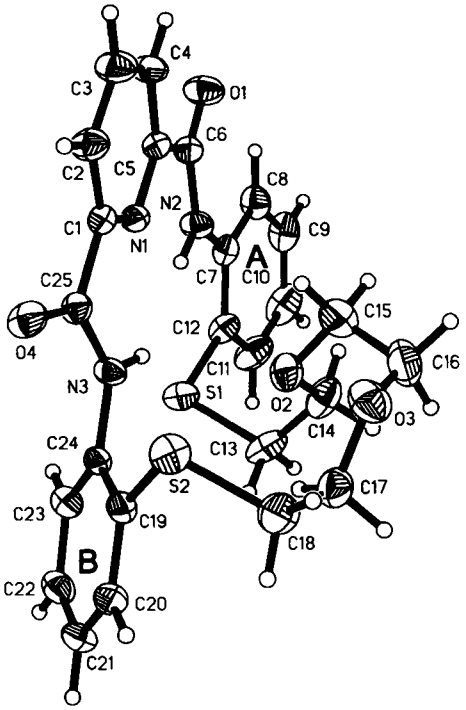

Abstract

$C_{25}H_{25}N_3O_4S_2$, monoclinic, $P12_1/n1$ (No. 14), $a = 11.516(1)$ Å, $b = 16.269(1)$ Å, $c = 12.899(1)$ Å, $\beta = 99.78(1)°$, $V = 2381.6$ Å^3, $Z = 4$, $R_{gt}(F) = 0.048$, $wR_{obs}(F^2) = 0.102$, $T = 293$ K.

Source of material

The title compound was prepared as reported in [1]. The design and synthesis of receptors for the development of fast estimation, removal and separation techniques for the target guests has drawn immense attention of the supramolecular chemists [2-6].

Discussion

During our studies on the development of silver selective ionophores, it has been found that the title compound does both, extracts and transports Ag^+ picrate selectively than Pb^{2+} and other metal ions [$sel._{ext.}$ (Ag^+/Pb^{2+}) = 564, $sel._{transp.}$ (Ag^+/Pb^{2+}) = 80] [7-10].

Its ^{13}C-NMR spectrum shows more than one signal for each C atom, it may exist as a mixture of two isomeric structures or may have a highly unsymmetrical structure with two unidentical halves. This high silver selectivity and an interesting ^{13}C-NMR spectrum prompted us to investigate the X-ray crystal structure of the compound.

Final structure of the molecule and its numbering scheme is shown in the figure. All the bond lengths and bond angles are normal. Group of atoms N1, N2, N3, S1 and S2, O2, O3, S1 form two approximate planes (mean deviation 0.07(1) Å and 0.11(1) Å, respectively). Dihedral angles between these planes is 73(1)°. Thus the macrocycle offers a L shaped cavity with seven potential donor atoms. All the three aromatic rings are planar (mean deviation < 0.01 Å) and the interplanar angles between pyridine and the phenylene ring A (C7 to C12) and Ring B (C19 to C24) are 6.8° and 42.8°, respectively. Ring A is almost parallel whereas ring B is rotated with respect to the pyridine ring. Torsion angles on both sides of the pyridine ring are similar except for rotations about amide nitrogen and the aromatic carbons carrying this group. C6–N2–C7–C12 is *anti* but C25–N3–C24–C19 is *gauche*, at the same time C6–N2–C7–C8 is almost *syn* but C25–N3–C24–C23 is more towards being *anti*. This rotation about N3–C24 takes ring B out of plane with the pyridine and ring A. The chain containing one 1,4-dioxa unit and two 1,4-thiaoxa units is in an extended conformation. The torsion angles sequence for the chain starting from the bond C7—C12 to C19—C24 may be written as *aggag-g-gagga*. A comparison of these with the torsion angles in crown ethers shows that all the three torsion angles about C—C bond alternate between + and – *gauche* but only half of the C–C–O–C and C–C–S–C are *anti*. Crown ethers exhibit all angles about C—C as *gauche* and those about C—O as *anti* [11]. This is probably due to the rigidity at the two ends of the thia-oxa chain. The torsion angles around O2 and O3 show that the lone pair of O2 is pointing towards the cavity but that of O3 is projected outwards. This indicates a possibility of intramolecular H-bonding interactions for O2 and intermolecular for O3. The non-bonding S—S distance is 6.5 Å. Both the amide nitrogens are involved in intramolecular H-bonding. N2 acts as a double donor and gives rise to a bifurcated H-bond between pyridine nitrogen N1 and S1. Similarly N3 donates a H-bond to N1 and O2. This involvement of amide hydrogens in H-bonding justifies the downfield shift of these protons in ^{1}H-NMR. Thus both of these hydrogens point inwards the cavity and the lone pairs of amide nitrogens pointing away from the cavity, are not available for the coordination to the metal ion. The packing of the molecule shows some important intermolecular C–H···O interactions. A plot of d versus θ was made to evaluate these weak C–H···O bonds [12,13]. The roughly inverse θ-d correlation in the plot is characteristic of H-bonding interactions. As predicted above, O3 has been found to be involved in the intermolecular H-bonding and O2 forms only intramolecular H-bonds. Various D, d, θ and φ values lie

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within the range found for such interactions and they also span much wider ranges of angles and distances than the closely grouped strong H-bond.These interactions are significant in forming a three dimensional network of molecules in the crystal structure. There also exist a face to face π-π interaction (3.74(1) Å) between the pyridine and the phenylene ring A of the two symmetry related molecules.

Table 1. Data collection and handling.

Crystal:	block, size 0.30 × 0.25 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.61 cm^{-1}
Diffractometer, scan mode:	Siemens P4, $2\theta/\omega$
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4426, 4203
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2793
$N(param)_{refined}$:	307
Program:	SHELXTL-PC [14]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(2B)	4e	0.5436(2)	0.0566(1)	0.8919(2)	0.054
H(3A)	4e	0.6648(2)	-0.0646(1)	0.8060(2)	0.047
H(2A)	4e	0.9404(2)	-0.0974(2)	1.0666(2)	0.060
H(3B)	4e	0.9452(3)	0.0082(2)	1.1882(2)	0.070
H(4A)	4e	0.7917(3)	0.1026(2)	1.1700(2)	0.061
H(8A)	4e	0.4265(3)	0.2322(2)	0.9873(2)	0.064
H(9A)	4e	0.2676(3)	0.3027(2)	0.8973(3)	0.076
H(10A)	4e	0.1697(3)	0.2566(2)	0.7385(3)	0.087
H(11A)	4e	0.2255(3)	0.1340(2)	0.6713(2)	0.081
H(13A)	4e	0.4900(3)	0.0066(2)	0.5816(2)	0.081
H(13B)	4e	0.4112(3)	0.0853(2)	0.5753(2)	0.081
H(14A)	4e	0.6014(3)	0.1278(2)	0.5856(3)	0.081
H(14B)	4e	0.5621(3)	0.1517(2)	0.6925(3)	0.081

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(15A)	4e	0.8225(3)	0.0734(2)	0.7975(3)	0.090
H(15B)	4e	0.7581(3)	0.1559(2)	0.7617(3)	0.090
H(16A)	4e	0.8053(3)	0.1279(2)	0.5894(3)	0.095
H(16B)	4e	0.9095(3)	0.1568(2)	0.6761(3)	0.095
H(17A)	4e	0.8552(3)	0.0056(2)	0.4942(2)	0.076
H(17B)	4e	0.7794(3)	-0.0246(2)	0.5774(2)	0.076
H(18A)	4e	1.0093(3)	-0.0839(2)	0.5778(3)	0.082
H(18B)	4e	0.8994(3)	-0.1295(2)	0.5153(3)	0.082
H(20A)	4e	0.7817(3)	-0.2452(2)	0.5260(2)	0.059
H(21A)	4e	0.5874(3)	-0.2812(2)	0.4731(2)	0.066
H(22A)	4e	0.4479(3)	-0.2418(2)	0.5716(2)	0.062
H(23A)	4e	0.5034(2)	-0.1677(2)	0.7243(2)	0.054

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	4e	0.40657(7)	0.01729(5)	0.73137(6)	0.0577(5)	0.0620(5)	0.0421(4)	0.0049(4)	0.0044(3)	-0.0070(4)
S(2)	4e	0.90991(6)	-0.15158(5)	0.69331(6)	0.0399(4)	0.0670(6)	0.0600(5)	0.0002(4)	0.0090(4)	-0.0005(4)
O(1)	4e	0.5876(2)	0.1647(1)	1.0828(2)	0.071(2)	0.058(1)	0.054(1)	0.013(1)	0.004(1)	-0.021(1)
O(2)	4e	0.6702(2)	0.0577(1)	0.7040(2)	0.061(1)	0.047(1)	0.062(1)	0.007(1)	0.007(1)	0.010(1)
O(3)	4e	0.9182(2)	0.0405(2)	0.6390(2)	0.060(1)	0.069(2)	0.084(2)	-0.011(1)	-0.000(1)	-0.004(1)
O(4)	4e	0.8418(2)	-0.1888(1)	0.9061(2)	0.073(1)	0.051(1)	0.047(1)	0.027(1)	-0.001(1)	0.004(1)
N(1)	4e	0.7006(2)	-0.0065(1)	0.9640(2)	0.039(1)	0.036(1)	0.032(1)	0.001(1)	0.0038(9)	0.001(1)
N(2)	4e	0.5260(2)	0.0982(1)	0.9272(2)	0.049(1)	0.040(1)	0.043(1)	0.011(1)	0.003(1)	-0.010(1)
N(3)	4e	0.7026(2)	-0.1102(1)	0.8066(2)	0.043(1)	0.033(1)	0.039(1)	0.007(1)	0.001(1)	-0.007(1)
C(1)	4e	0.7884(2)	-0.0611(2)	0.9765(2)	0.042(2)	0.036(2)	0.034(1)	0.001(1)	0.005(1)	0.004(1)
C(2)	4e	0.8808(2)	-0.0582(2)	1.0596(2)	0.049(2)	0.053(2)	0.044(2)	0.007(2)	-0.003(1)	-0.002(1)
C(3)	4e	0.8829(3)	0.0041(2)	1.1321(2)	0.051(2)	0.069(2)	0.049(2)	0.002(2)	-0.013(2)	-0.005(2)
C(4)	4e	0.7922(3)	0.0605(2)	1.1212(2)	0.057(2)	0.054(2)	0.039(2)	-0.005(2)	0.000(1)	-0.012(1)
C(5)	4e	0.7017(2)	0.0529(2)	1.0359(2)	0.044(2)	0.039(2)	0.032(1)	-0.003(1)	0.008(1)	-0.002(1)
C(6)	4e	0.5995(2)	0.1112(2)	1.0189(2)	0.050(2)	0.040(2)	0.035(2)	-0.001(1)	0.009(1)	-0.004(1)
C(7)	4e	0.4262(2)	0.1414(2)	0.8806(2)	0.043(2)	0.041(2)	0.044(2)	0.006(1)	0.014(1)	0.007(1)
C(8)	4e	0.3879(3)	0.2127(2)	0.9229(2)	0.056(2)	0.043(2)	0.063(2)	0.006(2)	0.020(2)	0.001(2)
C(9)	4e	0.2922(3)	0.2545(2)	0.8689(3)	0.064(2)	0.052(2)	0.081(2)	0.019(2)	0.030(2)	0.013(2)
C(10)	4e	0.2328(3)	0.2269(2)	0.7748(3)	0.064(2)	0.084(3)	0.072(2)	0.038(2)	0.019(2)	0.028(2)
C(11)	4e	0.2676(3)	0.1543(2)	0.7340(2)	0.062(2)	0.092(3)	0.048(2)	0.027(2)	0.005(2)	0.015(2)
C(12)	4e	0.3647(2)	0.1110(2)	0.7853(2)	0.047(2)	0.056(2)	0.040(2)	0.011(1)	0.012(1)	0.006(1)
C(13)	4e	0.4704(3)	0.0538(2)	0.6212(2)	0.074(2)	0.092(3)	0.036(2)	0.020(2)	0.010(2)	0.005(2)
C(14)	4e	0.5783(3)	0.1059(2)	0.6490(3)	0.080(2)	0.067(2)	0.059(2)	0.024(2)	0.025(2)	0.020(2)
C(15)	4e	0.7775(3)	0.1019(2)	0.7378(3)	0.091(3)	0.056(2)	0.074(2)	-0.010(2)	0.006(2)	-0.004(2)
C(16)	4e	0.8543(3)	0.1124(2)	0.6552(3)	0.087(3)	0.057(2)	0.092(3)	-0.020(2)	0.012(2)	0.009(2)
C(17)	4e	0.8591(3)	-0.0158(2)	0.5649(2)	0.062(2)	0.073(2)	0.055(2)	-0.018(2)	0.008(2)	0.007(2)
C(18)	4e	0.9264(3)	-0.0954(2)	0.5763(3)	0.064(2)	0.079(2)	0.067(2)	-0.012(2)	0.031(2)	-0.009(2)
C(19)	4e	0.7609(2)	-0.1820(2)	0.6570(2)	0.042(2)	0.033(1)	0.041(2)	0.001(1)	0.006(1)	0.001(1)
C(20)	4e	0.7257(3)	-0.2287(2)	0.5658(2)	0.063(2)	0.039(2)	0.047(2)	0.006(2)	0.016(2)	-0.006(1)
C(21)	4e	0.6095(3)	-0.2507(2)	0.5342(2)	0.071(2)	0.044(2)	0.048(2)	-0.009(2)	0.001(2)	-0.012(1)
C(22)	4e	0.5265(3)	-0.2274(2)	0.5931(2)	0.051(2)	0.044(2)	0.057(2)	-0.007(2)	0.000(2)	-0.003(2)
C(23)	4e	0.5597(2)	-0.1828(2)	0.6840(2)	0.043(2)	0.041(2)	0.050(2)	-0.002(1)	0.005(1)	-0.003(1)
C(24)	4e	0.6759(2)	-0.1604(2)	0.7159(2)	0.043(2)	0.026(1)	0.035(1)	0.001(1)	0.003(1)	-0.001(1)
C(25)	4e	0.7815(2)	-0.1270(2)	0.8938(2)	0.040(2)	0.039(2)	0.040(2)	0.004(1)	0.005(1)	0.004(1)

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