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A Convenient Route To Synthesize the Fully Conjugated Bimetallic Complex $(Bu_4N)_2\{tto[Ni(dmit)_2]\}$ (tto = Tetrathiooxalate, $C_2S_4^{2-}$, and dmit = 1,3-dithiole-2-thione-4,5-dithiolate, $C_3S_5^{2-}$) and the Crystal Structure of a New Crystal Form

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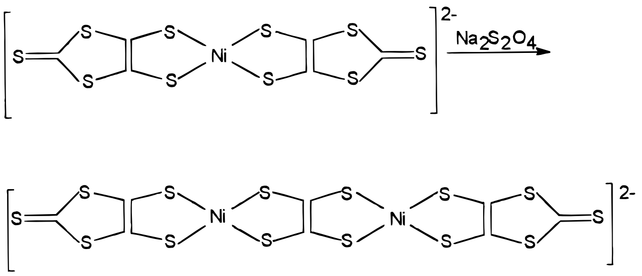
Introduction

Transition metal complexes with the dmit (1,3-dithiole-2-thione-4,5-dithiolate, $C_3S_5^{2-}$) ligand have received significant attention because of their metallic-like electronic properties.[1−7] These complexes form stable dianions, monoanions, and neutral species along with highly conducting complexes with a variety of "open-shell" and " closed-shell" cations. Several of their charge-transfer salts in this category exhibit superconducting properties. Examples include three complexes, $(NMe_4)_{0.5}[Ni(dmit)_2]$,[8] β-$(NMe_4)_{0.5}[Pd(dmit)_2]$,[9] and $[NMe_2Et_2]_{0.5}[Pd(dmit)_2]$,[10] containing closed-shell cations and four others, (TTF)-$[Ni(dmit)_2]_2$,[11] α- and α′-(TTF)$[Pd(dmit)_2]_2$,[12] and α-(EDT-TTF)-$[Ni(dmit)_2]$,[13] containing open-shell cations. The exciting properties of these complexes have been attributed to the ability of the planar acceptor ions to form close-packed segregated stacking arrangements. The incorporation of more heteroatoms, such as S or Se, into the periphery of the structure stabilizes the interactions via direct S···S or Se···Se overlap on the adjacent inter- and intrastack ions. Most preparations within this field utilize the tetraalkylammonium salts of $[M(dmit)_2]^{n-}$ (n = 2, 1) as starting material.

Scheme 1



Recently, Reynolds et al.[14−17] have reported a new series of chalcogen-rich, extensively conjugated and planar bimetallic complexes, $[C]_x\{tto[M(dmit)_2]\}$ [C = Bu_4N, Et_4N, Me_4N; tto = tetrathiooxalate, $C_2S_4^{2-}$; M = Cu(II), Ni(II)], in which the tto acts as the bridging ligand and the dmit as a capping ligand. This work opened up a new field for transition metal complexes with the dmit ligand. The fully conjugated bimetallic complex $(Bu_4N)_2\{tto[Ni(dmit)_2]\}$, which is the starting material for other conducting bimetallic complexes $[C]_x\{tto[Ni(dmit)_2]\}$,[16,17] has been prepared mainly on the basis of competitive reactions of the Ni^{2+} cation with tto and dmit dianions. Only a few of the bimetallic complexes containing dianion $\{tto[Ni(dmit)_2]\}^{2-}$ has been prepared because of the tedious work of synthesizing the precursor $(Bu_4N)_2\{tto[Ni(dmit)_2]\}$.[16,17] Here, we report a convenient and novel synthesis of $(Bu_4N)_2\{tto[Ni(dmit)_2]\}$ from $(Bu_4N)_2[Ni(dmit)_2]$. The crystal structure of a new crystal form of the complex is also presented.

Experimental Section

General Procedures and Methods. All reactions were completed under a dinitrogen atmosphere. $(Bu_4N)_2[Ni(dmit)_2]$ was prepared according to the literature method.[18,19] Other reagents were analytically pure and used without further purification.

Elemental analysis was performed using a Perkin-Elmer 240C analytical instrument. The IR spectrum was recorded on a Nicolet FTIR 170SX spectrophotometer. The UV−vis spectrum was recorded on a UV-3100 spectrophotometer.

Synthesis of $(Bu_4N)_2\{tto[Ni(dmit)_2]\}$ from $(Bu_4N)_2[Ni(dmit)_2]$ (Scheme 1). $(Bu_4N)_2[Ni(dmit)_2]$ (1.0 g, 1.11 mmol) was dissolved in MeCN (60 mL), and MeOH (3 mL) was added, to which a solution of $Na_2S_2O_4$ (2.0 g, 11.5 mmol) in 20 mL of H_2O was added. The resulting mixture was stirred for 12 h at 50 °C, and the color of the solution became brown. After filtration, excess dithionites and residues were removed. The filtrate was left standing overnight, and brown crystals were formed. The crystals were collected by filtration and then washed

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(1) Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayashi, A.; Clark, R. A.; Underhill, A. *Coord. Chem. Rev.* **1991**, *110*, 115.

(2) Olk, R.-M.; Olk, B.; Dietzsch, W.; Kirme, R.; Hoyer, E. *Coord. Chem. Rev.* **1992**, *117*, 99.

(3) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M. H. *Organic Superconductors (Including Fullerenes)*; Prentice Hall: Englewood Cliffs, NJ, 1992.

(4) Cassoux, P.; Valade, L. In *Inorganic Materials*; Bruce, D. W., O'Hare, D., Eds.; J. Wiley & Sons: Chichester, England, 1996; pp 3−17.

(5) Cassoux, P.; Valade, L. In *Inorganic Materials*; Bruce, D. W., O'Hare, D., Eds.; J. Wiley & Sons: Chichester, England, 1992; pp 1−58.

(6) You, X. Z.; Zhang, Y. In *Advances in Transition Metal Coordination Chemistry*; Che, C. M., Ed.; JAI Press Inc.: Greenwich, CT, 1996; pp 239−286.

(7) Faulmann, C.; Errami, A.; Donnadieu, B.; Malfant, I.; Legros, J. P.; Cassoux, P.; Rovira, C.; Canadell, E. *Inorg. Chem.* **1996**, *35*, 3856.

(8) Kajita, K.; Nishio, Y.; Moriyama, S.; Kato, R.; Kobayashi, H.; Sasaki, W. *Solid State Commun.* **1988**, *65*, 361.

(9) Kobayashi, A.; Kobayashi, H.; Miyamoto, A.; Kato, R.; Clark, R. A.; Underhill, A. E. *Chem. Lett.* **1991**, 2163.

(10) Kobayashi, H.; Bun, K.; Nato, T.; Kato, R.; Kobayashi, A. *Chem. Lett.* **1992**, 1909.

(11) Bousseau, M.; Valade, L.; Legro, J.-P.; Cassoux, P.; Garbauskas, M.; Interrante, L. V. *J. Am. Chem. Soc.* **1986**, *108*, 1908.

(12) Brossard, L.; Hurdeamn, H.; Ribault, M.; Valade, L.; Legros, J.-P.; Cassoux, P. *Synth. Met.* **1988**, *27*, B157.

(13) Tajima, H.; Inokuchi, M.; Kobayashi, A.; Ohta, T.; Kato, R.; Kabayashi, H.; Kuroda, H. *Chem. Lett.* **1993**, 1235.

(14) Piotraschke, J. J.; Pullen, A. E.; Abboud, K. A.; Reynlds, J. R. *Inorg. Chem.* **1995**, *34*, 4011.

(15) Pullen, A. E.; Zelter, S.; Olk, R.-M.; Hoyer, E.; Abboud, K. A.; Reynolds, J. R. *Inorg. Chem.* **1996**, *35*, 4420.

(16) Pullen, A. E.; Olk, R.-M.; Zeltner, S.; Hoyer, E.; Abboud, K. A.; Reynolds, J. K. *Inorg. Chem.* **1997**, *36*, 958.

(17) Pullen, A. E.; Zeltner, S.; Olk, R.-M.; Hoyer, E.; Abboud, K. A.; Reynolds, J. R. *Inorg. Chem.* **1997**, *36*, 4163.

(18) Steimecke, G.; Sieler, H. J.; Kirme, R.; Hoyer, E. *Phosphorus Sulfur Relat. Elem.* **1979**, *7*, 49.

(19) Valade, L.; Legros, J.-P.; Bousseau, M.; Cassoux, P. J.; Garbauskas, M.; Interrante, L. V. *J. Chem. Soc., Dalton Trans.* **1985**, 783.

10.1021/ic9902875 CCC: $19.00

Table 1. Crystallographic Data for $(Bu_4N)_2$\{tto[Ni(dmit)$_2$]\}

empirical formula	$C_{40}H_{72}N_2Ni_2S_{14}$
fw	1147.26
space group	$P2_1/c$
a, Å	9.9740(2)
b, Å	15.2622(3)
c, Å	17.9482(4)
β, deg	90.8125(8)
V, mm^{-3}	2731.89(10)
Z	2
T, K	293(2)
λ, Å×81	0.710 73
ρ_{calcd}, Mg/m^3	1.395
μ, mm^{-1}	1.254
GOF^a	0.885
R^b [$I > 2\sigma$]	0.052
R^b [all data]	0.129

[a] GOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ where F_o = observed structure factor, F_c = calculated structure factor, n = number of reflections, p = total number of parameters refined, w = weighing function. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$.

Table 2. Bond Lengths [Å] and Angles [deg] for $(Bu_4N)_2$\{tto[Ni(dmit)$_2$]\}^{a}

	Bond Length		
Ni(1)−S(7)	2.1618(12)	Ni(1)−S(6)	2.1648(10)
Ni(1)−S(4)	2.1667(12)	Ni(1)−S(5)	2.1744(10)
S(1)−C(17)	1.651(4)	S(2)−C(17)	1.735(4)
S(2)−C(18)	1.749(4)	S(3)−C(17)	1.729(4)
S(3)−C(19)	1.755(3)	S(4)−C(18)	1.744(3)
S(5)−C(19)	1.734(4)	S(6)−C(20)	1.703(4)
S(7)−C(20)$^{\#1}$	1.701(3)	N(1)−C(5)	1.519(4)
N(1)−C(1)	1.519(4)	N(1)−C(9)	1.520(5)
N(1)−C(13)	1.527(4)	C(1)−C(2)	1.514(5)
C(2)−C(3)	1.468(5)	C(3)−C(4)	1.500(5)
C(5)−C(6)	1.518(5)	C(6)−C(7)	1.525(5)
C(7)−C(8)	1.495(6)	C(9)−C(10)	1.523(5)
C(10)−C(11)	1.504(5)	C(11)−C(12)	1.516(6)
C(13)−C(14)	1.503(5)	C(14)−C(15)	1.514(5)
C(15)−C(16)	1.506(6)	C(18)−C(19)	1.332(5)
C(20)−C(20)$^{\#1}$	1.409(7)	C(20)−S(7)$^{\#1}$	1.701(3)
	Bond Angle		
S(7)−Ni(1)−S(6)	90.45(4)	S(7)−Ni(1)−S(4)	178.15(4)
S(6)−Ni(1)−S(4)	87.96(4)	S(7)−Ni(1)−S(5)	87.99(4)
S(6)−Ni(1)−S(5)	175.01(4)	S(4)−Ni(1)−S(5)	93.67(4)
C(17)−S(2)−C(18)	97.4(2)	C(17)−S(3)−C(19)	97.35(19)
C(18)−S(4)−Ni(1)	101.49(14)	C(19)−S(5)−Ni(1)	101.16(14)
C(20)−S(6)−Ni(1)	104.63(13)	C(20)$^{\#1}$−S(7)−Ni(1)	105.03(14)
C(5)−N(1)−C(1)	106.8(2)	C(5)−N(1)−C(9)	110.7(3)
C(1)−N(1)−C(9)	110.4(3)	C(5)−N(1)−C(13)	110.9(3)
C(1)−N(1)−C(13)	110.3(3)	C(9)−N(1)−C(13)	107.8(3)
C(2)−C(1)−N(1)	116.0(3)	C(3)−C(2)−C(1)	111.5(3)
C(2)−C(3)−C(4)	115.8(4)	C(6)−C(5)−N(1)	116.0(3)
C(5)−C(6)−C(7)	111.7(3)	C(8)−C(7)−C(6)	115.3(4)
N(1)−C(9)−C(10)	115.4(3)	C(11)−C(10)−C(9)	112.7(3)
C(10)−C(11)−C(12)	110.7(4)	C(14)−C(13)−N(1)	115.9(3)
C(13)−C(14)−C(15)	113.0(3)	C(16)−C(15)−C(14)	112.7(4)
S(1)−C(17)−S(3)	123.9(2)	S(1)−C(17)−S(2)	123.4(3)
S(3)−C(17)−S(2)	112.7(2)	C(19)−C(18)−S(4)	121.3(3)
C(19)−C(18)−S(2)	116.4(3)	S(4)−C(18)−S(2)	122.3(2)
C(18)−C(19)−S(5)	122.3(3)	C(18)−C(19)−S(3)	116.2(3)
S(5)−C(19)−S(3)	121.4(3)	C(20)$^{\#1}$−C(20)−C(7)$^{\#1}$	119.0(4)
C(20)$^{\#1}$−C(20)−(6)	119.5(3)	S(7)$^{\#1}$−C(20)−S(6)	121.5(2)

[a] Symmetry transformation used to generate equivalent atoms, denoted $^{\#1}$, is −*x*, −*y*, −*z*.

thoroughly with water and MeOH to remove dithionites and other impurities. Finally, the product was recrystallized from CH_3CN. Yield: 0.40 g (66%). Anal. Calcd for $C_{40}H_{72}N_2S_{14}Ni_2$: C, 41.87; H, 6.34, N, 2.44. Found: C, 42.02, H, 6.24, N, 2.51. IR (KBr, cm^{-1}): $\nu_{C=C}$ 1452.8, $\nu_{C=S}$ 1078. UV−vis [CH_3CN, nm (log ϵ in parentheses)]: 379 (4.58), 495 (4.10), 1045 (4.53).

Single crystals suitable for X-ray determination were obtained by slowly diffusing diethyl ether into a DMF solution of the complex.

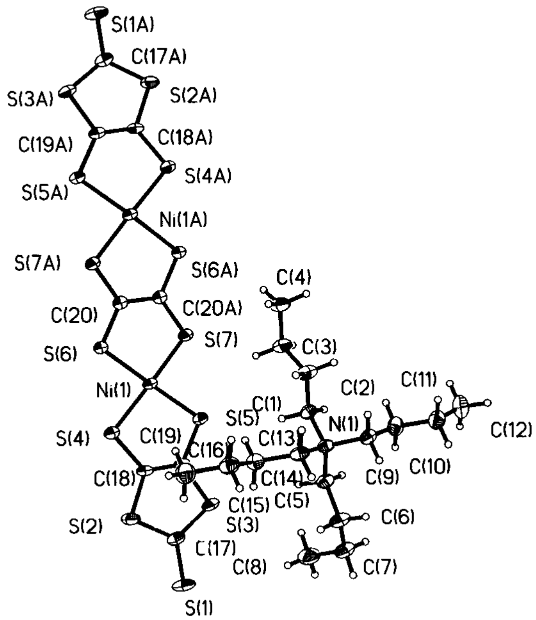

Figure 1. Molecular structure and numbering scheme for $(Bu_4N)_2$\{tto[Ni(dmit)$_2$]\} with 50% probability ellipsoids.

X-ray Crystallography. A brown crystal needle of the $(Bu_4N)_2$\{tto[Ni(dmit)$_2$]\} with approximate dimensions of 0.36 mm × 0.22 mm × 0.14 mm was mounted in air. The intensity data were collected at 293(2) K on a Siemens SMART CCD diffractometer with a detector distance of 4 cm and a frame exposure time of 30 s. The structure was resolved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXTL software[20] with 6513 unique absorption-corrected (empirical, $T_{min} = 0.661$, $T_{max} = 0.844$) reflections. All non-hydrogen atoms were anisotropically refined. The refinement converged at $R = 0.052$, and $R_w = 0.097$ for a total of 262 parameters and 6513 observed reflections with $I > 2.0\ \sigma(I)$. The crystallographic data are listed in Table 1.

The selected bond distances and bond angles are listed in Table 2. Complete crystallographic data, atomic coordinates, thermal parameters, and bond distances and angles are gathered in Supporting Information.

Results and Discussion

Synthesis of $(Bu_4N)_2$\{tto[Ni(dmit)$_2$]\} from $(Bu_4N)_2$[Ni(dmit)$_2$]. The tetrabutylammonium salt of $[Ni(dmit)_2]^{2-}$ is a good starting material for the preparation of either nonintegral oxidation state complexes such as the superconducting $[Me_4N]_{0.5}$-$[Ni(dmit)_2]_2$ or donor−acceptor compounds such as the superconducting $[TTF][Ni(dmit)_2]_2$.[1−7] In this paper, we used it as the precursor to prepare the fully planar bimetallic complex $(Bu_4N)_2$\{tto[Ni(dmit)$_2$]\}.

Although it has long been proposed that tto^{2-} is the precursor to $C_3S_5^{2-}$ in the reduction (chemical and electrochemical) of CS_2,[21,22] which has been confirmed recently,[23] the reverse conversion of $C_3S_5^{2-}$ to tto^{2-} has not been suggested or investigated. We first observed the transformation from $C_3S_5^{2-}$ to tto^{2-} and confirmed that $C_3S_5^{2-}$ is the precursor to tto^{2-}. That is, they could transform to each other under certain conditions, even though both $C_3S_5^{2-}$ and tto^{2-} dianions are in coordination states.

This unexpected reaction occurred during the course of synthesizing some alkylation derivatives of nickel complexes

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[20] *SHELXTL Reference Manual*, version 5; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1996.
[21] Jeroschewski, P. *Z. Chem.* **1981**, *21*, 412.
[22] Jeroschewski, P.; Hansen, P. *Sulfur Rep.* **1986**, *7*, 1.
[23] Breiter, J. G.; Chou, J.-H.; Rauchfuss, T. B. *Inorg. Chem.* **1998**, *37*, 2080.

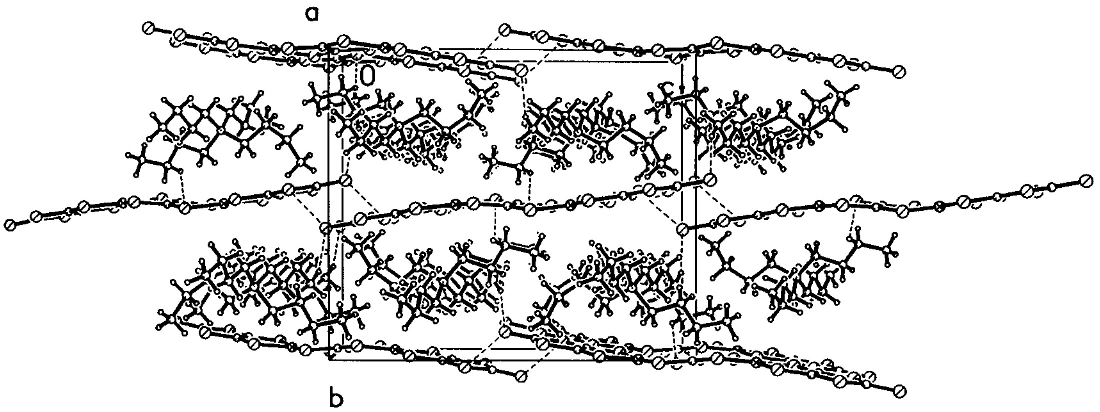

Figure 2. Packing diagram with unit cell labels of $(Bu_4N)_2\{tto[Ni(dmit)_2]\}$ showing sheets containing complex dianions and tetrabutylammonium cations.

with the dmit ligand.[24] The bromine compounds did not react with $Ni(dmit)_2^{2-}$ and did not take part in the reaction of the conversion of $(Bu_4N)_2[Ni(dmit)_2]$ to $(Bu_4N)_2\{tto[Ni(dmit)_2]\}$.

By comparison to the previous method,[16] this is a convenient and effective route to synthesize $(Bu_4N)_2\{tto[Ni(dmit)_2]\}$. In our preparation procedure, the tedious process to synthesize the compound $(Et_4N)_2$tto was avoided; therefore, formation of the polymeric byproduct $[Ni(tto)]_n$ was not observed. Thus, the yield is up to 66%, which is higher than that of the method using $(Et_4N)_2$tto (41%). Since $(Bu_4N)_2\{tto[Ni(dmit)_2]\}$ is the precursor for other conducting bimetallic complexes $[C]_x\{tto[Ni(dmit)_2]\}$, including nonintegral oxidation state complexes and donor−acceptor compounds,[16,17] the new method will facilitate research on them.

Structure of the New Crystal Form of $(Bu_4N)_2\{tto[Ni(dmit)_2]\}$. The space group ($P2_1/c$) of the new crystal form is different from the one that Reynolds et al. reported earlier ($P2_12_12_1$).[16] The atomic labeling scheme of the dianion is shown in Figure 1. In the molecule, two Ni(dmit) fragments are linked by the side-on coordination of a tto ligand. The C20−C20A bond of the tto ligand is 1.409(7) Å shorter than that in the structure of previous crystal form[16] [1.416(7) Å] and that in the isolated dianionic tto ligand [24] [1.461(11) Å]. The π system of the bridging tto ligand is highly delocalized and results in a planar structure. The Ni−S [2.1633(11) Å] and C−S [1.702(4) Å] bond lengths are comparable to those found for the previous crystal form, which are 2.158(4) and 1.706(12) Å, respectively. The coordination about the d^8 Ni(II) metal centers is square-planar as expected. The S−Ni−S bond angles with the tto bridging ligand [90.45(4) and 87.98(4)°, respectively] are very close to 90°. The whole complex is not perfectly planar, and the dihedral angle between the planes of the bridging tto and the capping dmit is 16.5°.

The view from the *a* axis (Figure 2) shows a significant amount of one-dimensional nonbonding orbital interactions of thioxo−thiole [$S1\cdots S3^{\#}$, 3.604(4) Å] of the dianionic units resulting in each bimetallic unit interacting with two adjacent bimetallic units.

The cations interact with the dianionic units by $C-H\cdots S$ hydrogen bonds. Each dianionic unit is in contact with the adjacent cations via four $C-H\cdots S$ hydrogen bonds [$C(3)-H(3A)\cdots S(7)^{\#2}$, 3.651(4) Å; $C(12)-H(12A)\cdots S(1)^{\#3}$, 3.792(5) Å].[25] Thus, the crystal packing is characterized by sheets of separating cations and dianions with nonbonding $S\cdots S$ interaction and hydrogen bonds in two dimensions. There is no interaction observed among the sheets.

Summary

A novel route for the conversion of $(Bu_4N)_2[Ni(dmit)_2]$ to $(Bu_4N)_2\{tto[Ni(dmit)_2]\}$ is reported here. This provides a much more efficient way of synthesizing $(Bu_4N)_2\{tto[Ni(dmit)_2]\}$ than the literature method. During the process, the conversion of $dmit^{2-}$ to tto^{2-} was realized for the first time. This new synthesis should facilitate further research on the conducting bimetallic complexes $[C]_x\{tto[Ni(dmit)_2]\}$. In addition, a new crystal form of $(Bu_4N)_2\{tto[Ni(dmit)_2]\}$ was determined by X-ray crystallographic analysis.

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Supporting Information Available: X-ray crystallographic file in CIF format for the structure determination of $(Bu_4N)_2\{tto[Ni(dmit)_2]\}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Vries, N. D.; Reedijk, J. *Inorg. Chem.* **1991**, *30*, 3700.

(25) Lund, H.; Hoyer, E.; Groenbaeck-Hazell, R. *Acta Chem. Scand., Ser. B* **1982**, *36*, 207.