ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2014, Vol. 40, No. 6, pp. 407–412. © Pleiades Publishing, Ltd., 2014.

Synthesis, Crystal Structures, and Biological Property of Dinuclear Oxovanadium(V) Complexes Derived from Tridentate Schiff Bases[1]

X. J. Zhao[a], Q. Peng[b], and L. W. Xue[a,*]

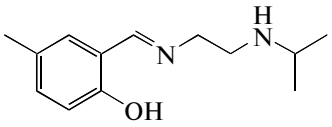
[a]*College of Chemistry and Chemical Engineering, Pingdingshan University, Pingdingshan Henan, 467000 P.R. China*
[b]*College of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang Henan, 464000 P.R. China*
**e-mail: pdsuchemistry@163.com*
Received January 27, 2014

Abstract—A pair of structurally similar dinuclear oxovanadium(V) complexes, $[VO_2L^1]_2$ (**I**) and $[VO_2L^2]_2$ (**II**), where L^1 and L^2 are the mono-anionic form of 2-[(2-isopropylaminoethylimino)methyl]-4-methylphenol (HL^1) and 4-fluoro-2-[(2-isopropylaminoethylimino)methyl]phenol (HL^2), respectively, have been synthesized and characterized by elemental analysis, FT-IR spectra, and single crystal X-ray determination. The crystal of **I** is monoclinic: space group $P2_1/c$, $a = 12.528(1)$, $b = 12.266(1)$, $c = 9.432(1)$ Å, $\beta = 104.814(3)°$, $V = 1401.2(3)$ Å^3, $Z = 2$. The crystal of **I** is monoclinic: space group $P2_1/n$, $a = 12.3128(5)$, $b = 6.5124(3)$, $c = 17.1272(7)$ Å, $\beta = 105.863(1)°$, $V = 1321.1(1)$ Å^3, $Z = 2$. The V···V distances are 3.210(1) Å in **I** and 3.219(1) Å in **II**. The V atoms in the complexes are in octahedral coordination. Biological assay indicates that complex **II**, bearing fluoro-substitute groups, has stronger antimicrobial activity against most bacteria than complex **I** which bearing methyl-substitute groups.

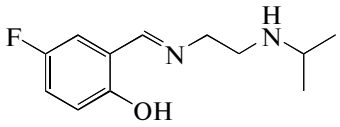
DOI: 10.1134/S1070328414060116

INTRODUCTION

Vanadium complexes with various types of organic ligands have received remarkable attention in recent years for their biological and medicinal applications [1–4]. Among the ligands, Schiff bases are considered as a very important class of organic compounds which have wide applications in many biological aspects. Some Schiff bases were reported to possess antibacterial, antifungal and antitumor activities [5–7]. Moreover, it is well known that some biological activities, when administered as metal complexes, are being increased [8, 9]. The literature reveals that oxovanadium complexes with Schiff bases have been less studied. Zhang and coworkers have reported that halosubsituted compounds usually have effective biological properties [10]. We report herein two new dimeric oxovanadium(V) complexes, $[VO_2L^1]_2$ (**I**) and $[VO_2L^2]_2$ (**II**), where L^1 and L^2 are the mono-anionic form of 2-[(2-isopropylaminoethylimino)methyl]-4-methylphenol (HL^1) and 4-fluoro-2-[(2-isopropylaminoethylimino)methyl]phenol (HL^2), respectively.



(HL^1)



(HL^2)

EXPERIMENTAL

Materials and methods. 5-Methylsalicylaldehyde, 5-fluorosalicylaldehyde, and *N*-isopropylethane-1,2-diamine were purchased from Fluka. Other reagents and solvents were analytical grade and used without further purification. Elemental (C, H, and N) analyses were made on a PerkinElmer Model 240B automatic analyzer. The vanadium content was determined as

[1] The article is published in the original.

V_2O_5. IR spectra were recorded on an IR-408 Shimadzu 568 spectrophotometer.

Synthesis of HL^1 and HL^2. *N*-Isopropylethane-1,2-diamine (1.02 g, 0.01 mol) and 5-methylsalicylaldehyde (1.36 g, 0.01 mmol) for HL^1 or 5-fluorosalicylaldehyde (1.40 g, 0.01 mmol) for HL^2 were mixed in methanol (30 mL). The mixtures were stirred at reflux for 30 min and the solvent was evaporated to give yellow oily products of HL^1 and HL^2.

For $C_{13}H_{20}N_2O$ (HL^1)

anal. calcd., %:	C, 70.87;	H, 9.15;	N, 12.72.
Found, %:	C, 70.62;	H, 9.23;	N, 12.85.

For $C_{12}H_{17}FN_2O$ (HL^2)

anal. calcd., %:	C, 64.26;	H, 7.64;	N, 12.49.
Found, %:	C, 64.37;	H, 7.55;	N, 12.60.

Synthesis of the complexes. The Schiff bases (0.5 mmol each) in methanol (20 mL) was added with stirring to $VOAacac)_2$ (0.5 mmol, 0.13 g) in methanol (10 mL). The mixtures were stirred at refluxed for 30 min to give yellow solution. The solution was left still at room temperature in air to give yellow block-shaped single crystals, which were collected by filtration and dried in vacuum containing anhydrous $CaCl_2$. The yields were over 70%.

For $C_{26}H_{38}N_4O_6V_2$ (**I**)

anal. calcd., %:	C, 51.66;	H, 6.34;	N, 9.27;	V, 16.85.
Found, %:	C, 51.51;	H, 6.40;	N, 9.18;	V, 17.02.

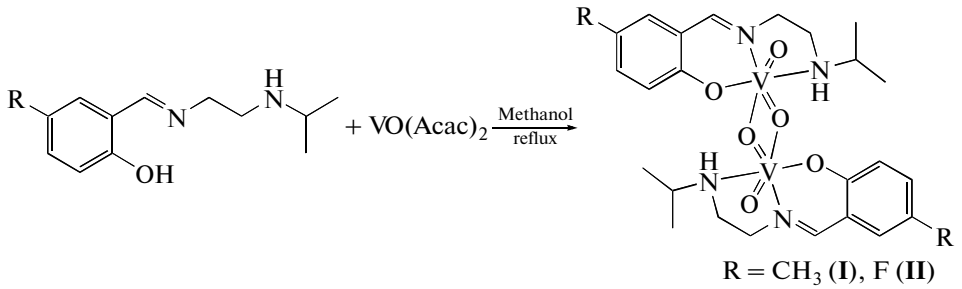
For $C_{24}H_{32}F_2N_4O_6V_2$ (**II**)

anal. calcd., %:	C, 47.07;	H, 5.27;	N, 9.15;	V, 16.64.
Found, %:	C, 47.21;	H, 5.33;	N, 9.06;	V, 16.83.

X-ray crystal determination. Data were collected from selected crystals mounted on glass fibers. The data for the complexes were processed with SAINT [11] and corrected for absorption using SADABS [12]. Multi-scan absorption corrections were applied with ψ scans [13]. The structures were solved by direct method using the SHELXS-97 program and refined by full-matrix least-squares techniques on F^2 using anisotropic displacement parameters [14]. All non-hydrogen atoms were refined anisotropically. The amino H atoms in the complexes were located from difference Fourier maps and refined isotropically with N–H distances restrained to 0.90(1) Å. The remaining hydrogen atoms were placed at the calculated positions. The crystallographic data for the complexes are listed in Table 1. Selected bond lengths and angles are given in Table 2. Hydrogen bonding information is listed in Table 3. Supplementary materials have been deposited with the Cambridge Crystallographic Data Centre (nos. 960528 (**I**) and 960527 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The synthesis of the complexes is shown in Scheme:



Scheme.

The molecular structures of the complexes **I** and **II** are shown in Fig. 1. Both complexes crystallize as centrosymmetric dinuclear structures, with the inversion center located at the midpoint of the two V atoms. The V···V distances are 3.210(1) Å in **I** and 3.219(1) Å in **II**. The V atom in each complex is in an octahedral coordination with the phenolate O, imine N, and amine N atoms of the Schiff base ligand and one oxo O atom defining the equatorial plane, and with two oxo O atoms occupying the two axial positions. The V atoms deviate from the least-squares planes defined by the four equatorial donor atoms by 0.357(1) Å in **I** and 0.350(1) Å in **II**. The V–O and V–N coordinate bond lengths in the complexes are comparable to each other and also comparable to the corresponding values observed in other similar oxovanadium(V) complexes

Table 1. Crystallographic data and structure refinement summary for complexes **I** and **II**

Parameter	Value	
	I	**II**
Habit, colour	Block, yellow	Block, yellow
Formula weight	604.48	612.42
Temperature, K	298(2)	298(2)
Crystal size, mm	0.27 × 0.23 × 0.23	0.20 × 0.20 × 0.17
Radiation, λ, Å	MoK_α (0.71073)	MoK_α (0.71073)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions:		
a, Å	12.528(1)	12.3128(5)
b, Å	12.266(1)	6.5124(3)
c, Å	9.432(1)	17.1272(7)
β, deg	104.814(3)	105.863(1)
V, Å^3	1401.2(3)	1321.1(1)
Z	2	2
ρ_{calcd}, mg cm^{-3}	1.433	1.540
F(000)	632	632
Absorption coefficient, mm^{-1}	0.713	0.768
θ Range for data collection, deg	2.36–25.50	2.47–25.50
Index ranges	$-13 \le h \le 15$, $-14 \le k \le 12$, $-11 \le l \le 11$	$-14 \le h \le 14$, $-7 \le k \le 7$, $-20 \le l \le 20$
Reflections collected	12454	12092
Independent reflections	2605	2443
Data/restraints/parameters	2008/1/179	2173/1/178
Final R indices ($I > 2\sigma(I)$)	0.0342	0.0289
R indices (all data)	0.0839	0.0768
Goodness-of-fit	1.047	1.070
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	0.255, –0.236	0.218, –0.204

Table 2. Coordinate bond distances (Å) and angles (deg) for complexes **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
		I	
V(1)–O(1)	1.919(2)	V(1)–O(2)	1.607(2)
V(1)–O(3)	1.660(2)	V(1)–N(1)	2.157(2)
V(1)–N(2)	2.184(2)	V(1)–O(3*A*)	2.408(2)
		II	
V(1)–O(1)	1.926(1)	V(1)–O(2)	1.612(1)
V(1)–O(3)	2.445(1)	V(1)–N(1)	2.155(2)
V(1)–N(2)	2.155(2)	V(1)–O(3*B*)	1.658(1)
Angle	ω, deg	Angle	ω, deg
		I	
O(2)V(1)O(3)	107.00(8)	O(2)V(1)O(1)	100.67(8)
O(3)V(1)O(1)	99.13(7)	O(2)V(1)N(1)	99.72(8)
O(3)V(1)N(1)	151.74(7)	O(1)V(1)N(1)	84.52(7)
O(2)V(1)N(2)	94.20(8)	O(3)V(1)N(2)	92.37(7)
O(1)V(1)N(2)	157.58(7)	N(1)V(1)N(2)	76.44(7)
O(2)V(1)O(3*A*)	170.67(7)	O(3)V(1)O(3*A*)	77.36(7)
O(1)V(1)O(3*A*)	86.55(6)	N(1)V(1)O(3*A*)	74.89(6)
N(2)V(1)O(3*A*)	77.22(6)		
		II	
O(2)V(1)O(3*B*)	108.85(7)	O(2)V(1)O(1)	100.13(6)
O(3*B*)V(1)O(1)	98.83(6)	O(2)V(1)N(1)	96.42(6)
O(3*B*)V(1)N(1)	153.48(6)	O(1)V(1)N(1)	84.10(6)
O(2)V(1)N(2)	94.66(6)	O(3*B*)V(1)N(2)	92.67(6)
O(3)V(1)N(2)	157.16(6)	N(1)V(1)N(2)	76.98(6)
O(2)V(1)O(3)	169.99(6)	O(3)V(1)O(3*B*)	78.35(6)
O(1)V(1)O(3)	85.27(5)	N(1)V(1)O(3)	75.63(5)
N(2)V(1)O(3)	77.78(5)		

* Symmetry codes: (*A*) $2-x, 1-y, -z$; (*B*) $-x, 2-y, -z$.

Table 3. Hydrogen bond distances (Å) and bond angles (deg) for complexes **I** and **II***

D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
		I		
N(2)–H(2)···O(1)^{i}	0.90(1)	2.34(2)	3.072(2)	139(2)
N(2)–H(2)···O(3)^{i}	0.90(1)	2.33(2)	2.871(2)	119(2)
		II		
N(2)–H(2)···O(1)^{ii}	0.90(1)	2.36(2)	3.062(2)	135(2)
N(2)–H(2)···O(3)	0.90(1)	2.36(2)	2.897(2)	118(2)

* Symmetry codes for: ^{i} $2-x, 1-y, -z$; ^{ii} $-x, 2-y, -z$.

Table 4. MIC values (μg/mL) for antimicrobial activities of the compounds

Compound	*Staphylococcus aureus*	*Escherichia coli*	*Candida albicans*
HL^1	32	128	>512
HL^2	16	32	128
I	8	16	64
II	2	8	64
Tetracycline	0.32	2.12	>512

with Schiff bases [15–18]. There exist two N–H···O hydrogen bonds between the two $[VO_2L]$ units, which might contribute to the formation of dimeric structures. Crystal structures of the complexes are stabilized by hydrogen bonds, as shown in Fig. 2.

In the infrared spectra of the free Schiff bases, the weak ν(O–H) bands were observed at about 3350–3480 cm^{-1}. The bands are absent after chelation, suggesting the coordination through the deprotonated form. In the infrared spectra of the free Schiff bases, the ν(C=N) bands are at about 1647–1651 cm^{-1}, which are located at lower wave numbers for the complexes, 1637 cm^{-1} for **I** and 1639 cm^{-1} for **II**, indicating that the Schiff bases are coordinated to the Vatoms through the azomethine N atoms. The mid-

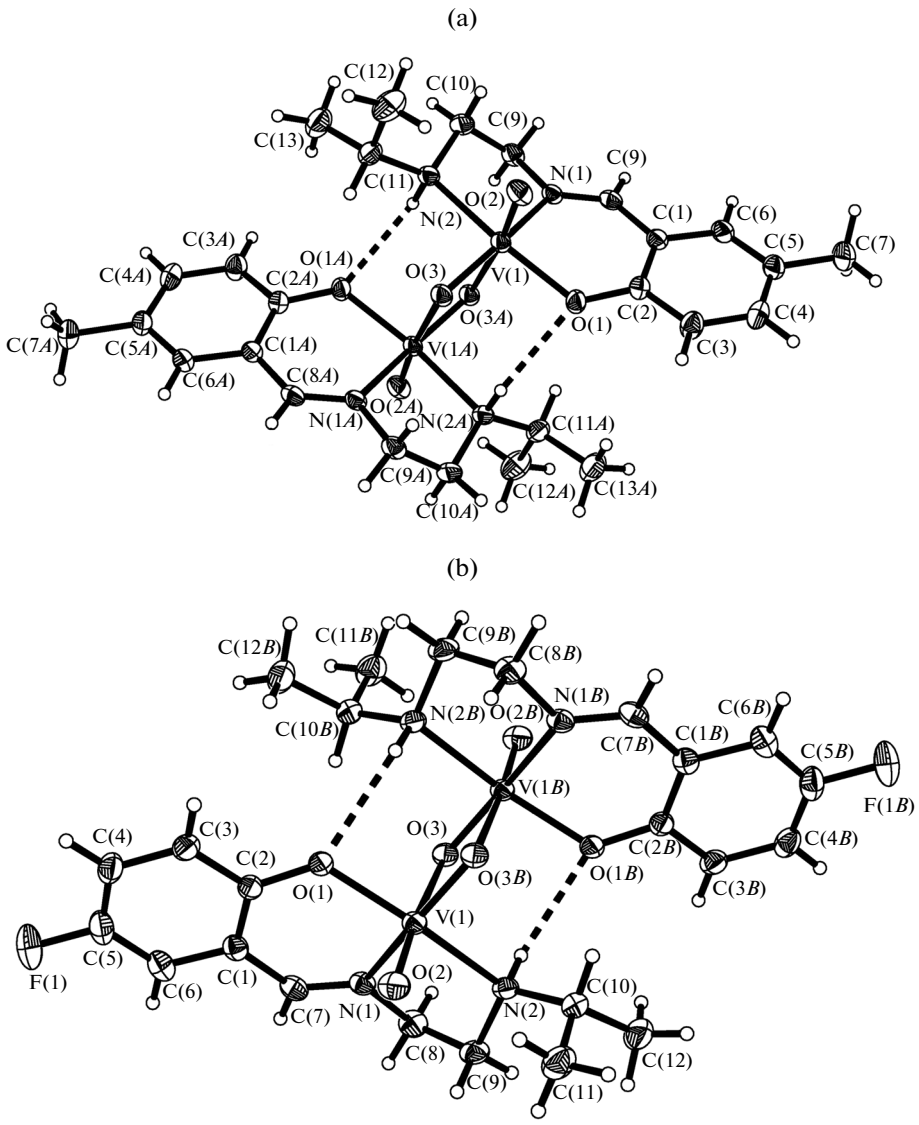


Fig. 1. Molecular structure of **I** (a) and **II** (b) at 30% probability displacement. Hydrogen bonds are drawn as dotted lines.

dle ν(C–O) bands in the spectra of the complexes are located at 1123 cm^{-1} for **I** and 1127 cm^{-1} for **II**. The characteristic ν(V=O) and ν(V–O) bands can be monitored at about 940 and 450 cm^{-1}, respectively.

Qualitative determination of antimicrobial activity was done using the disk diffusion method [19, 20]. The results are summarized in Table 4. Generally, the complexes show greater antimicrobial activities against *Staphylococcus aureus, Escherichia coli*, and *Candida albicans*, when compared to the free Schiff bases. Generally, this is caused by the greater lipophilic nature of the complex than the ligand. Such increased activity of the metal chelates can be explained on the basis of chelating theory [21]. On chelating, the polarity of the metal atoms will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of the metal atoms with donor atoms. Further, it increases the derealization of *p*-electrons over the whole chelate ring and enhances the lipophilicity of the complex. This increased lipophilicity enhances the penetration of the complex into the lipid membrane and blocks the metal binding sites on enzymes of microorganisms. In addition, it is obvious that complex **II** has stronger activities than complex **I**. Detailed study on the relationship between the structures of the Schiff bases and complexes with their activities can conclude that the fluoro-substitute groups can increase the biological properties.

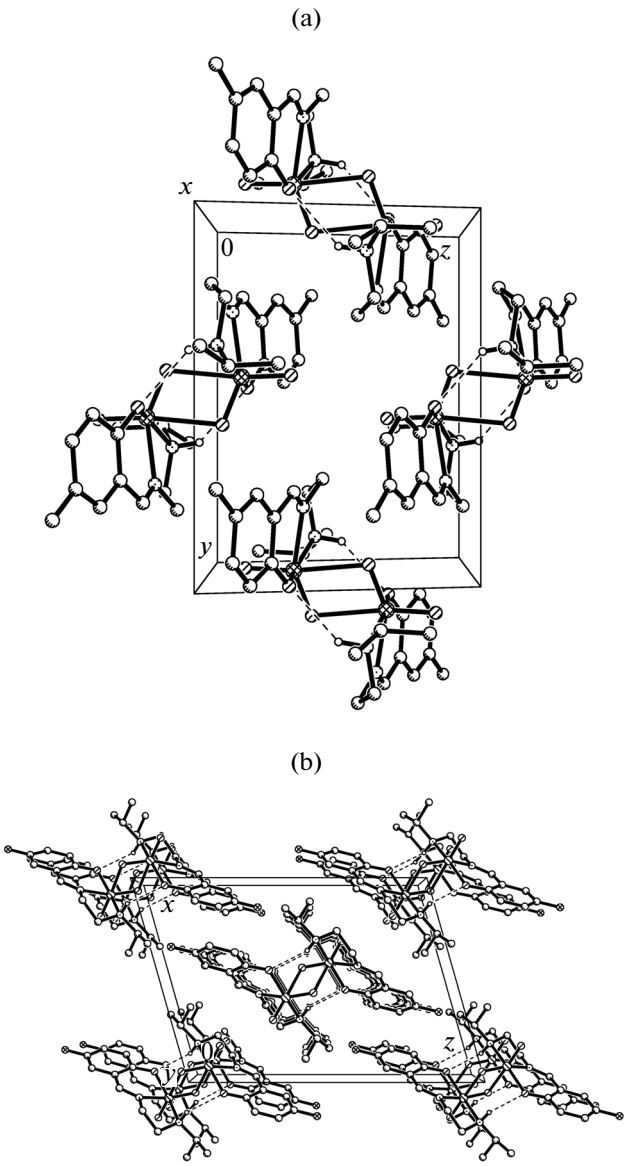


Fig. 2. Crystal packing structure of **I** (a) and **II** (b).

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation of China (nos. 20676057 and 20877036) and the Top-class Foundation of the Pingdingshan University (no. 2008010).

REFERENCES

1. Li, X., Lah, M.S., and Pecoraro, V.L., *Inorg. Chem.*, 1988, vol. 27, no. 25, p. 4657.
2. Monga, V., Thompson, K.H., Yuen, V.G., et al., *Inorg. Chem.*, 2005, vol. 44, no. 8, p. 2678.
3. Rio del, D., Galindo, A., Tejedo, J., et al., *Inorg. Chem. Commun.*, 2000, vol. 3, no. 1, p. 32.
4. Grüning, C., Schmidt, H., and Rehder, D., *Inorg. Chem. Commun.*, 1999, vol. 2, no. 1, p. 57.
5. Sonmez, M., Celebi, M., and Berber, I., *Eur. J. Med. Chem.*, 2010, vol. 45, no. 5, p. 1935.
6. Mohamed, G.G., Omar, M.M., and Ibrahim, A.A., *Eur. J. Med. Chem.*, 2009, vol. 44, no. 12, p. 4801.
7. Sinha, D., Tiwari, A.K., Singh, S., et al., *Eur. J. Med. Chem.*, 2008, vol. 43, no. 1, p. 160.
8. Bagihalli, G.B., Avaji, P.G., Patil, S.A., et al., *Eur. J. Med. Chem.*, 2008, vol. 43, no. 12, p. 2639.
9. Sun, Y.-X., *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, 2006, vol. 36, no. 8, p. 621.
10. Zhang, M., Xian, D.-M., Li, H.-H., et al., *Aust. J. Chem.*, 2012, vol. 65, no. 4, p. 343.
11. *SMART and SAINT, Area Detector Control and Integration Software*, Madison (WI, USA): Bruker Analytical X-ray Instruments Inc., 1997.
12. Sheldrick, G.M., *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, Göttingen (Germany): Univ. of Göttingen, 1997.
13. North, A.C.T., Phillips, D.C., and Mathews, F.S., *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 1968, vol. 24, no. 3, p. 351.
14. Sheldrick, G.M., *SHELXL-97, Program for the Refinement of Crystal Structures*, Göttingen (Germany): Univ. of Göttingen, 1997.
15. Duncan, C.A., Copeland, E.P., Kahwa, I.A., et al., *Dalton Trans.*, 1997, no. 6, p. 917.
16. Mokry, L.M. and Carrano, C.J., *Inorg. Chem.*, 1993, vol. 32, no. 26, p. 6119.
17. Mondal, S., Mukherjee, M., Dhara, K., et al., *Cryst. Growth Des.*, 2007, vol. 7, no. 9, p. 1716.
18. Abe, Y., Lyoda, A., Seto, K., et al., *Eur. J. Inorg. Chem.,* 2008, no. 13, p. 2148.
19. Barry, A., *Antibiotics in Laboratory Medicine*, Lorian V., Ed., Baltimore: Williams and Wilkins, 1991, p. 1.
20. Rosu, T., Negoiu, M., Pasculescu, S., et al., *Eur. J. Med. Chem.*, 2010, vol. 45, no. 2, p. 774.
21. Searl, J.W., Smith, R.C., and Wyard, S., *J. Proc. Phys. Soc.*, 1961, vol. 78, no. 505, p. 1174.